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# Preparation of Durable Ceramic Coatings by Spray Pyrolysis

FINAL REPORT - PHASE II

by

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## SUMMARY

This final report included the work performed in DSS Spray Pyrolysis Phase II of the program from July 1, 1983, to February 29, 1984. The overall results of the program (Phase I and Phase II) can be summarized, as follows:

- A coating process was developed for the deposition of $ZrO_2$ films on glass and other metal substrates such as carbon steel, stainless steel, aluminum, TiC coated carbon steel, nickel plated mild steel from n-butyl zirconate solution at a furnace temperature range of 500 to 600°C.

- $ZrO_2$ films prepared by this spray pyrolysis process improved the abrasion resistance of aluminum and the high temperature oxidation resistance of TiC coated carbon steel substrates.

- The maximum coating thickness obtained by this spray pyrolysis process was about 1.6 μ. Higher coating thickness cannot be achieved without the film losing its transparent characteristics.

- Thin films of amorphous alumina on glass and metallic substrates can be deposited by spray pyrolysis of aluminum sec-butoxide in toluene. The properties of these coatings have not been evaluated under this program.



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## 1. INTRODUCTION

The use of surface coating provides an important means of increasing the life of engineering materials and other components by reducing wear, corrosion and impurity permeation. Surface coatings also find applications in many electronic devices as a result of the increasing demand for thin films in the semiconductor industry. A wide range of techniques are available for preparing thin protective coatings. Of these, the spray pyrolysis process is one of the attractive techniques considering its simplicity, economics and easy operation.

On September 21, 1982, the Ontario Research Foundation initiated a research and development program under the sponsorship of the Department of Energy, Mines and Resources. The purpose of the program was to demonstrate the feasibility of depositing durable ceramic coatings using the spray pyrolysis technique (ORF Proposal P-3774-G, Revised, May 31, 1982).

This program was completed in two phases. The first phase of the program which involved demonstrating the feasibility of producing durable coatings by the spray pyrolysis technique was completed in June 1983. During this phase it was demonstrated that adherent transparent coatings could be produced by the spray pyrolysis of alkoxide precursors of $ZrO_2$ and $TiO_2$. An interim report covering the nine-month period of Phase I was reviewed on July 17, 1983.

Phase II of the program was started on July 1, 1983 and was extended to February 29, 1984. The work during Phase II involved the deposition of $ZrO_2$ coatings on industrially important substrate materials as well as the characterization and property evaluation of such coatings. The industrial potential of the $ZrO_2$ coatings prepared by the spray pyrolysis technique was investigated as well. The deposition of mixed alumina-zirconia coatings and alumina coatings was also demonstrated during Phase II of the program.

This document in conjunction with the Phase I interim report comprise data, experimental results and experience acquired from the project.

Parts of the experimental data generated under this program were presented at the 1984 Canadian Ceramic Society meeting in Toronto. The technical information presented at this meeting included the preparation and property evaluation of zirconia film on glass substrates.

## 2. OBJECTIVES

The objectives of this program were:

i) To develop a method for the application of abrasion resistant coatings using the spray pyrolysis technique.

ii) To evaluate the coatings produced by the spray pyrolysis technique, for increasing the abrasion resistance.

iii) To assess the industrial potential of abrasion resistant coatings produced by the spray pyrolysis technique.

## 3. MAJOR TASKS

The program was carried out in two phases. The first phase was started in September 1982 and was completed in June 1983. The final report for Phase I of the program was completed which included the literature review on coating technology and the experimental results achieved in Phase I. Phase II of the program was initiated on July 1, 1983 and was completed on February 29, 1984.

The major tasks for both phases I and II are listed below:

### 3.1 Phase I - Feasibility

The program during this phase consisted of the following major tasks:

3.1.1 A literature survey of the reagents used for film deposition, the methods for substrate preparation, the properties of the coatings (specifically abrasion resistance) and their industrial potential.

3.1.2 The selection of coating compositions to be produced by spray pyrolysis.

3.1.3 The selection of reagents for the spray solutions.



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3.1.4 The development of solution formulations.

3.1.5 The adaptation of the existing spray system and technology at the Ontario Research Foundation to make it compatible with the solutions formulated under 3.1.4.

3.1.6 The selection and preparation of substrates for film deposition.

3.1.7 The deposition of films using spray technology.

3.1.8 The evaluation of the films deposited in terms of adhesion, hardness, abrasion resistance, thickness and microstructure.

3.1.9 The parameters of the spray pyrolysis process will be modified when the coatings examined under 3.1.8 show poor characteristics.

3.1.10 The results of the investigation will be critically examined in light of published data in a Final Report for Phase I.

3.2 Phase II - Coating Development

The following major tasks were completed to optimize the properties of the coatings:

3.2.1 The composition of the coatings which show promise will be modified to further enhance their properties.

3.2.2 The spray solutions will be modified to yield coatings with the compositions specified under 3.2.1.

3.2.3 The spray system will be adapted to accommodate the altered solution formulations.

3.2.4 The substrates will be modified to optimize the properties of the coatings. A representative selection of substrates will be made to scan the range of potential industrial applications.

3.2.5 The improved coatings will be deposited.

3.2.6 The improved coatings will be evaluated in terms of adhesion, hardness, abrasion resistance, thickness and microstructure.

3.2.7 The industrial potential of the abrasion resistant coatings produced by spray pyrolysis will be evaluated.

3.2.8 The results obtained during Phase II of the program will be correlated with the data of Phase I and the work of both phases will be discussed with reference to the existing literature in a comprehensive final report.



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## 4. PROGRAM STATUS

As of February 29, 1984, the program is completed on schedule and within budget. No assistance or guidance from the Crown is needed at this time.

All major tasks have been completed as of February 29, 1984, pending the acceptance of this final report by the scientific authority for this project.

## 5. PROGRAM RESULTS

During Phase II of the program, efforts were directed towards the evaluation and improvement of the $ZrO_2$ film on glass and other commercially important substrates. Further work on the development of an alumina film was also carried out.

### 5.1 $ZrO_2$ Films

Process parameters for the $ZrO_2$ coating process developed in Phase I were modified and optimized. Samples were prepared for the evaluation of coating properties which included the thickness, the abrasion resistance, the hardness value, the microstructure and the optical transmittance and reflectance.

#### 5.1.1 Modification of Process Parameters

The coating parameters of the $ZrO_2$ spray pyrolysis process were optimized and modified. These parameters included the coating temperature, spray schedule and heat treatment duration. Soda-lime glass substrates were used in this investigation. A temperature recorder was installed to monitor the temperature of the sample during the spray operation. A temperature profile of the substrate during the spray operation is presented in Figure 1. The computer program for the control system of the spray pyrolysis facility was upgraded and modified for multiple spray coating.

The data of this investigation are summarized in Appendix A. The modified computer program is also included with this appendix.



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The results of this task can be summarized as follows:

- The best coating temperature for glass substrates was found to be 550 C. $^{O}$At higher temperatures, glass tended to crack and break more frequently during the spray process. Lower temperatures produced non-adhesive and powdery films.

- The best coating schedule was a 5-second spray followed by a 5-minute heat treatment in the furnace at the coating temperature. The spray duration depended on the cooling behaviour of the substrate. The temperature of the substrate must be maintained near the decomposition temperature of the solution. The decomposition temperature of butyl zirconate as determined by thermogravimetric analysis (TGA, see Appendix B) was between 250 and 400$^{O}$C (Fig. 2).

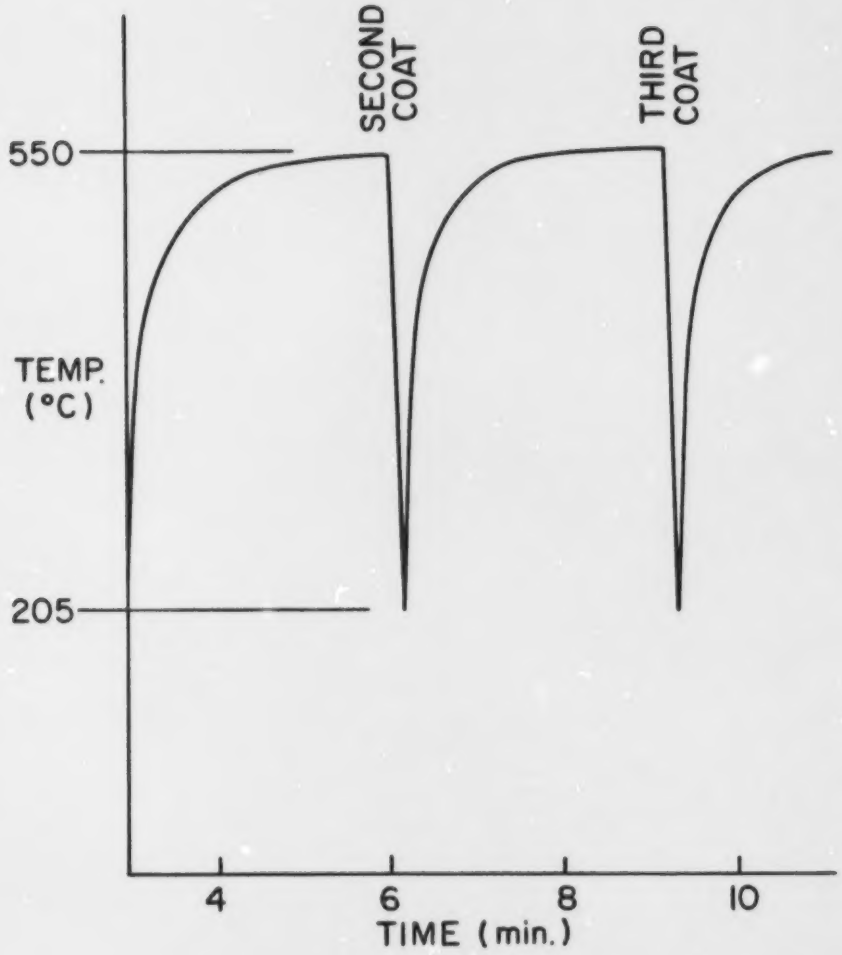
- The coating thickness can be increased by increasing the number of the spray sequences. Up to 20 coats (5-second spray and 5 minute heat treatment per coat) were achieved with some reduction in the transparent characteristics of the film.

- The coating solution was 100% n-butyl zirconate.

### 5.1.2 Evaluation of Different Substrates

Soda-lime glass samples were extensively used as the substrates for $ZrO_2$ coating because of their availability, low cost and chemical inertness. To extend the potential usefulness of the zirconia coatings prepared by spray pyrolysis, a number of commercially important substrates were selected and tested. These included:

- Carbon steel
- Stainless steel 304 and 310
- Enamelled steel
- Aluminum
- Nickel plated mild steel
- TiC coated carbon steel




TEMPERATURE PROFILE OF SODA LIME GLASS SAMPLE.

Figure 1



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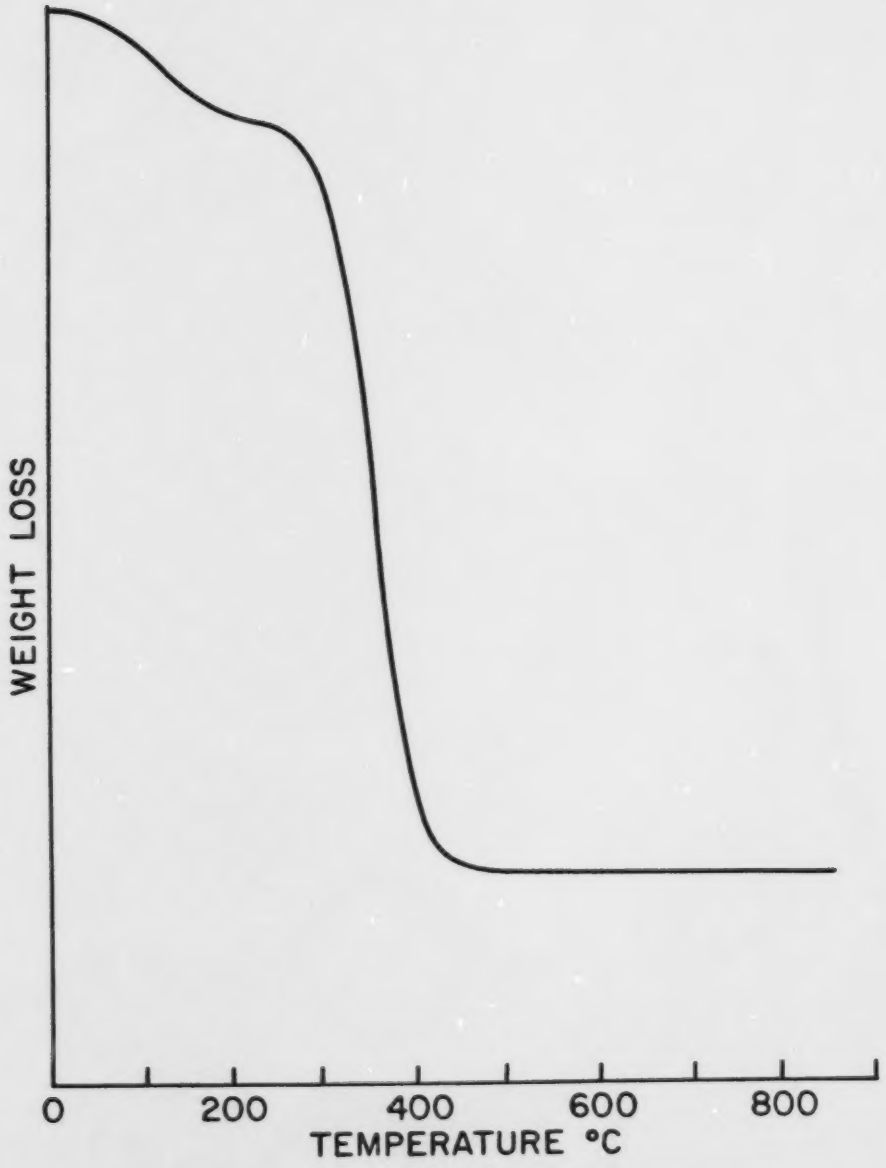


Fig. 2 THERMOGRAVIMETRIC ANALYSIS OF BUTYL ZIRCONATE.



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Due to the high thermal conductivity of the metals and resultant rapid heat losses, the spray duration was reduced from five seconds to two seconds. Thus, the spray schedule for a metal substrate was a spray of two seconds followed by a two-minute heat treatment. In order to ensure that the coating temperature was reached, the metal samples must be heated in the furnace at this temperature for about five minutes prior to the spraying process.

(i) Glass

The $ZrO_2$ film deposited on glass at 500-600$^{o}$C was transparent and well adherent. The properties of the $ZrO_2$ films on glass substrates were investigated in detail and reported in section 5.1.3.

(ii) Aluminum Substrates

Transparent $ZrO_2$ films were successfully deposited onto aluminum substrates (1100-H14 Aluminum Sheet-Ideal Metal & Alloys of Canada) using the spray pyrolysis technique. The range of the coating temperature evaluated was from 400$^{o}$C to about 550$^{o}$C. As shown in Table C1 (Appendix C) poor coatings with dull colour and cracks were obtained at temperatures below 550$^{o}$C; while at temperatures higher than 550$^{o}$C, aluminum started to deform. The best temperature for a clear transparent $ZrO_2$ coating on aluminum was determined to be 550$^{o}$C.

(iii) $ZrO_2$ Coatings on Enamelled Steel Substrates

N-butyl zirconate which was used earlier for the deposition of $ZrO_2$ coatings on glass was also used for the deposition of transparent coatings on enamelled steel (Table C2, Appendix C).

As on glass substrates, adherent transparent coatings can be obtained at furnace temperatures of 500 to 600$^{o}$C. X-ray powder patterns show that as in the case of glass cubic or tetragonal $ZrO_2$ could be obtained. The x-ray spectrum also shows the pattern of $TiO_2$ (anatase). It is surmised that this pattern can be attributed to $TiO_2$ in the enamel on the steel.



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(iv) Stainless Steel - 304 & 310

Due to their high temperature resistance characteristics, stainless steels 310 and 304 were selected as the candidates for zirconia coating by spray pyrolysis. The operating furnace temperature was between 400 to 700°C. The coating procedure was as follows:

- Wash the stainless steel samples (4"x 8"x 1/8")
- Dip in 35% phosphoric acid solution for about 10 minutes
- Rinse with water and acetone
- Dry in oven at 80°C for about 10 minutes.
- Spray with n-butyl zirconate (Kay-Fries Ind.)

Zirconia coatings were successfully deposited onto 310 and 304 stainless steel substrates. The optimum temperature range for 310 stainless steel was found to be from 500 to 600°C. At higher temperature, oxidation of stainless steel occurred which impeded the coating process while at lower temperatures, the film was powdery and poor in adherence (Tables C3 and C4, Appendix C).

(v) Carbon Steel

$ZrO_2$ films were successfully deposited onto carbon steel substrates. Carbon steel samples (4"x7", 16 gauge - Dans Welding & Fabricating, Ont.) were prepared according to the following procedures:

- Wash the sample with detergent
- Rinse with water
- Dip in 20% phosphoric acid for about 5 minutes
- Rinse with water
- Rinse with acetone
- Dry in oven at 100°C

Spraying trials were conducted to evaluate and to optimize the coating parameters. The testing data are presented in Table C5 (Appendix C). The best coating temperature for a clear adherent thin $ZrO_2$ film on carbon steel appeared to be 550°C.



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(vi) Nickel Plated Mild Steel

Thin layers of electroless nickel were plated on mild steel samples to improve the oxidation resistance of mild steel during the coating operation. Films with Newton-ring structures were obtained at the temperature range of 500-550°C. The most promising temperature for $ZrO_2$ coatings on nickel surface was found to be 550°C. The experimental data for this investigation are presented in Table C6 (Appendix C). The micrographs of the coated and uncoated samples are shown in Figs. C1 and C2 (Appendix C).

(vii) TiC Coated Carbon Steel

This investigation was carried out to determine the compatibility of $ZrO_2$ films with TiC substrate surfaces. TiC coated carbon steel samples were obtained (SCI Coating Ltd, Ont.) and were prepared for spraying experiments.

Spray pyrolysis produced a clear thin film with good adherence on the TiC coated carbon steel substrate at a temperature of 550°C. The experimental data are given in Table C7 (Appendix C). The coated and uncoated TiC substrates are shown in Figs. 3 and 4, respectively.

The results of this evaluation strongly indicate that $ZrO_2$ films can be deposited by spray pyrolysis on many clean and smooth substrates which can withstand the coating temperature of about 500-550°C. This is an attractive property as the $ZrO_2$ film can be used as a primer coat for many ceramic coatings which require proper undercoats to improve the adhesion strength of the top coatings.

5.1.3 Property Evaluation of $ZrO_2$ Film - Glass Substrate

Several important properties of $ZrO_2$ films deposited on glass substrates were measured and evaluated. These properties were abrasion resistance, hardness, film microstructure composition and thickness. Optical properties such as transmittance and reflectance in the visible and infrared regions of the spectrum, respectively, were also included. Samples for testing were prepared using the best coating parameters, a coating

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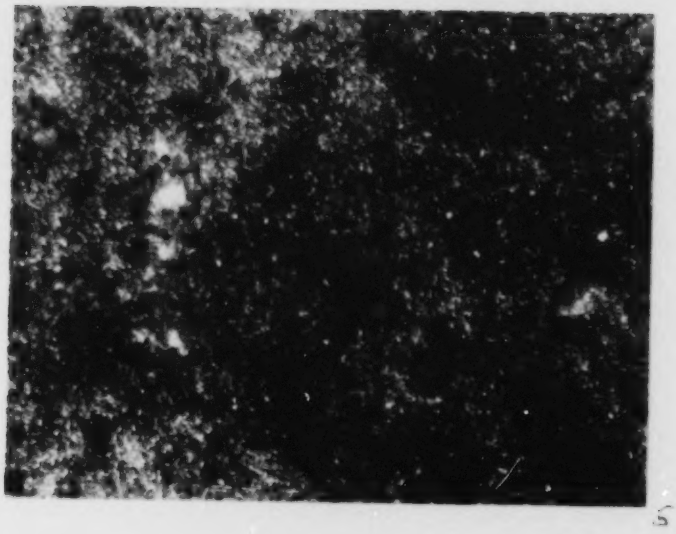

Figure 3: $ZrO_2$ Film on TiC Carbon Steel
(Temperature 500° - 3 coats - x370)

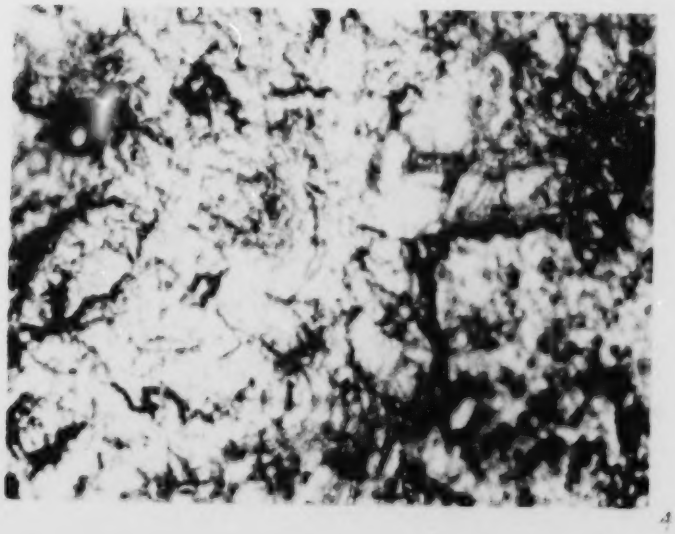

Figure 4 : Uncoated Virgin TiC Carbon Steel
(x370)

schedule of a five-second spray followed by a five-minute heat treatment in the furnace at 550°C. The spray sequence was repeated as many times as required to obtain the desired coating thickness.

5.1.3.1 Film Structure and Composition

The structure and composition of $ZrO_2$ films on glass were studied and reported in detail in the Phase I final report. The x-ray and energy dispersive x-ray analysis spectra as shown in Figs. 5 and 6, respectively, indicated the presence of tetragonal/cubic $ZrO_2$ on the glass surface. The composition of the film was about 52% $ZrO_2$ (Table 1). Other components such as $SiO_2$, CaO, and $Na_2O$ can be attributed to the glass substrate. A small amount of $HfO_2$ was also observed, presumably from an impurity in the butyl zirconate solution.

5.1.3.2 Abrasion Resistance

(i) Method of Measurement

The abrasion resistance of thin oxide films is difficult to measure due to the thinness of the film and the non-existence of an applicable standard for abrasion measurements for thin ceramic coatings. The ASTM standards consulted were ASTM D668-81, D168-81, D158-72 and D4060-81. Out of these, the most suitable ASTM Standard appeared to be D4060-81 (Appendix D).

A systematic test program was carried out to evaluate and optimize the major operating parameters which affected the wear index results of the coated and uncoated samples. Taber abrasion machine and uncoated glass samples (4"x4") were used in this investigation. The operating parameters investigated were:

- Procedures for weight measurement
- Abrader wheel
- Cycling schedules



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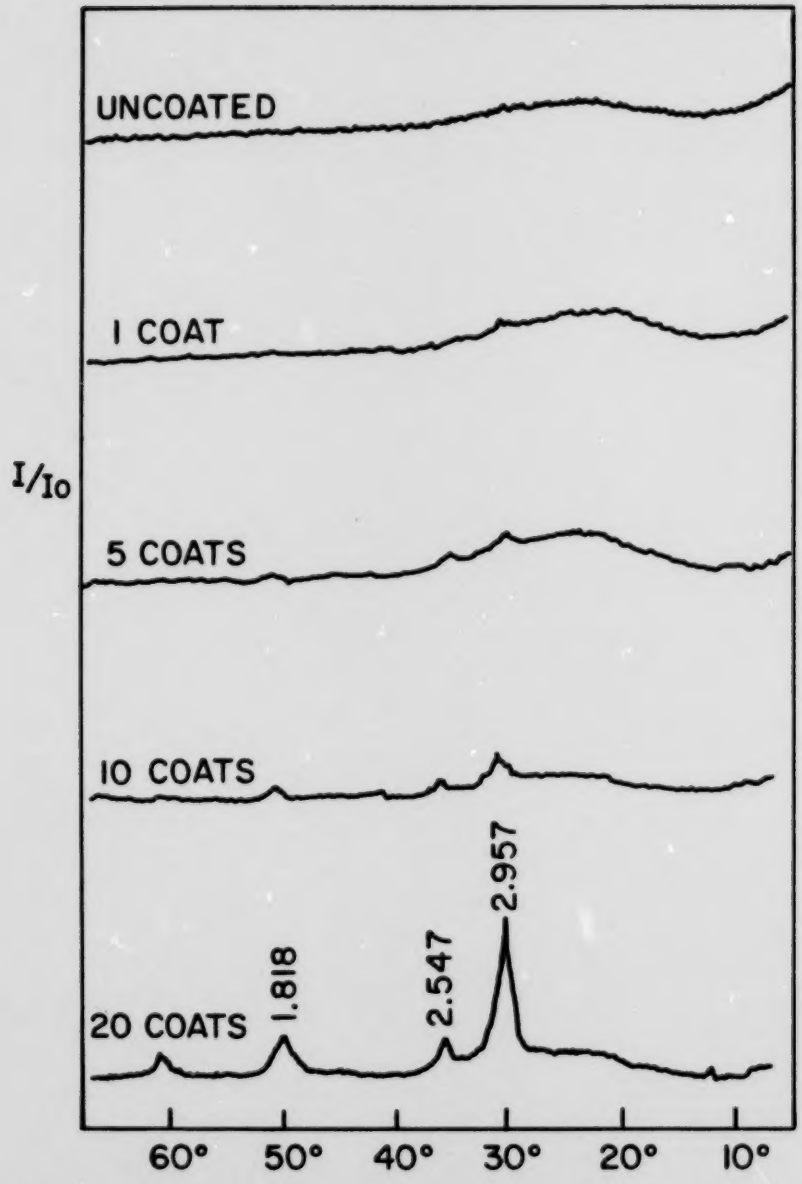


Fig.5 X-RAY ANALYSIS OF COATED AND UNCOATED GLASS SAMPLES.



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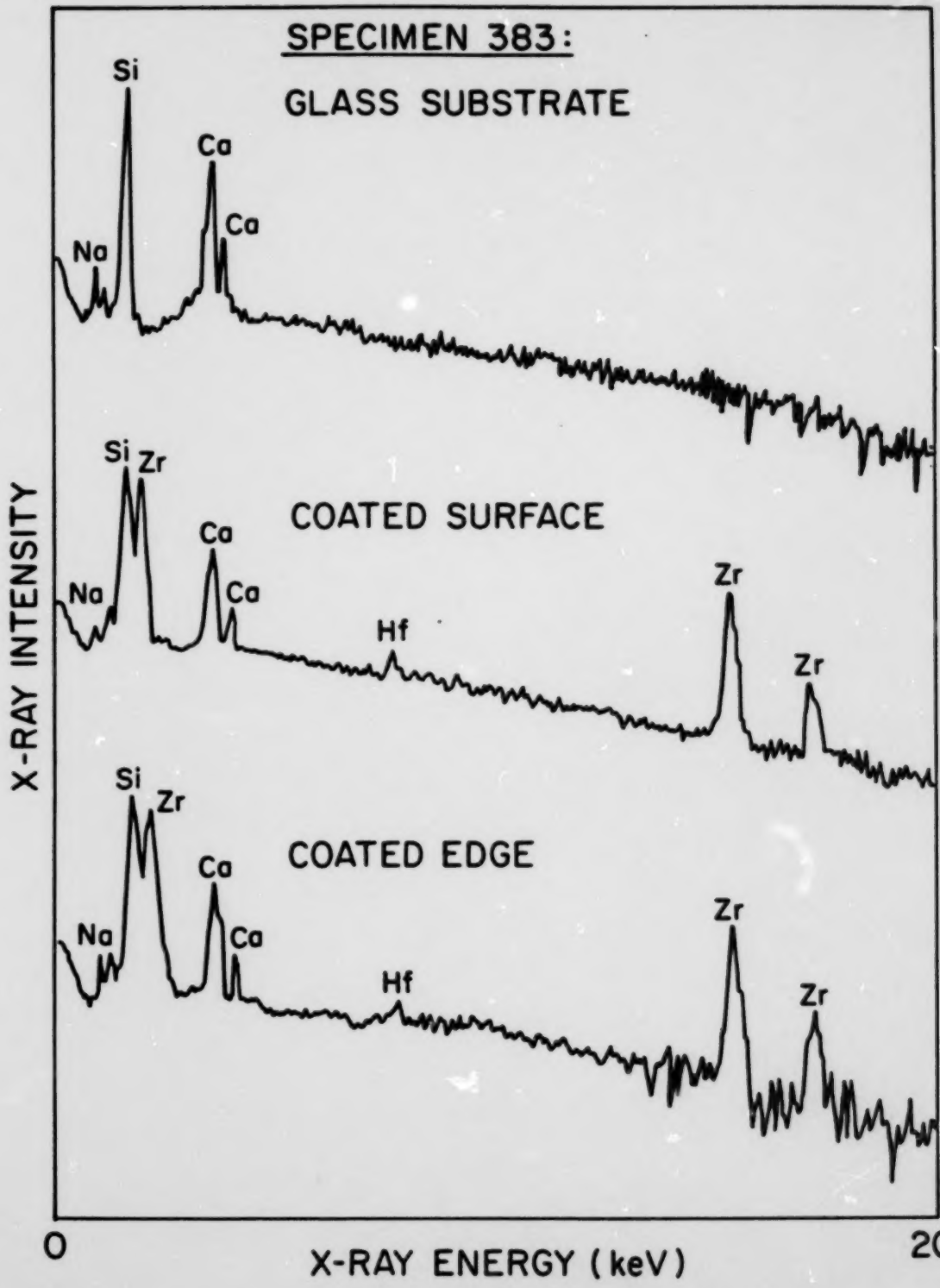


Fig. 6 E.D. X-RAY SPECTRA OF COATED AND UNCOATED GLASS SAMPLES.



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TABLE 1

ED X-Ray Analysis of $ZrO_2$ Film on Glass

SPECTRUM 517DN2GN1E FEB. 3, 1984

| | |
|---|---|
| ACCELERATING VOLTAGE | 30.0 KEV |
| INCIDENCE ANGLE | 60.0 DEGREES |
| EFFECTIVE TAKE-OFF ANGLE | 54.0 DEGREES |

STANDARDLESS EDS ANALYSIS
(ZAF CORRECTIONS VIA MAGIC V)

| ELEMENT & LINE | K-RATIO | WEIGHT PERCENT | PRECISION 2 SIGMA | OXIDE FORMULA | OXIDE PERCENT | NO. OF CATIONS IN FORMULA |
|---|---|---|---|---|---|---|
| NA KA | 0.0012 | 0.22 | 0.01 | NA2O | 0.29 | 0.0085 |
| MG KA | 0.0025 | 0.30 | 0.01 | MGO | 0.49 | 0.0110 |
| SI KA | 0.2397 | 16.44 | 0.07 | SIO2 | 35.17 | 0.5256 |
| CL KA | 0.0005 | 0.07 | 0.01 | CL | 0.07 | 0.0000 |
| CA KA | 0.0834 | 6.00 | 0.06 | CAO | 8.39 | 0.1344 |
| FE KA | 0.0047 | 0.22 | 0.01 | FEO | 0.29 | 0.0036 |
| CU KA | 0.0021 | 0.09 | 0.01 | CUO | 0.11 | 0.0013 |
| ZR LA | 0.6343 | 39.13 | 0.19 | ZRO2 | 52.86 | 0.3851 |
| SN LA | 0.0124 | 0.99 | 0.04 | SNO2 | 1.26 | 0.0075 |
| HF LA | 0.0192 | 0.91 | 0.05 | HFO2 | 1.07 | 0.0046 |
| O * | | 35.64 | | | | |
| TOTAL | | | | | 100.00 | 1.0815 |

NUMBER OF CATIONS CALCULATED ON BASIS OF 2 OXYGEN ATOMS.

* DETERMINED BY STOICHIOMETRY



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Different operating conditions were applied in order to modify and optimize the most suitable techniques for abrasion measurement of $ZrO_2$ coatings on glass prepared by the spray pyrolysis method.

A detailed description of the determination of the operating parameters is given in Appendix D. On the basis of the results the following operating parameters have been established.

(a) Pretreatment of the samples with detergent, rinsing with acetone and drying at 80°C.
(b) A waiting period of half an hour between the pre-treatment and measurement of the sample weight.
(c) Wheel type: H-10.
(d) Load: 1,000 g
(e) Cycling Schedule: 35.

(ii) Abrasion Evaluation of $ZrO_2$ Coated Glass Samples

The data of the abrasion tests presented in Table D3 (Appendix D) were calculated and statistical analysis was applied. The data sets are compared using the alternative hypothesis in which $\bar{X}_u$ (the average wear index of the uncoated samples) is less than $\bar{X}_c$ (the average wear index of $ZrO_2$ coated samples) with 70 to 99% of confidence (Table D4).

The average wear indices of coated and uncoated glass samples are plotted in Figure 7. In this figure, the uncoated glass samples have the lowest wear index which means that the $ZrO_2$ coatings lower the abrasion resistance of the window glass samples. Also, the abrasion resistance of the coated glass decreases as the coating thickness increases.

5.1.3.3 Hardness Values

The hardness of the $ZrO_2$ films on glass substrates was measured using a miniload (100g) microhardness tester equiped with a Knoop indentor. Three indentation points were measured for each specimen. The average data of these results were plotted in Fig. 8. As shown in this figure, the $ZrO_2$ film lowered the hardness value of soda-lime glass.



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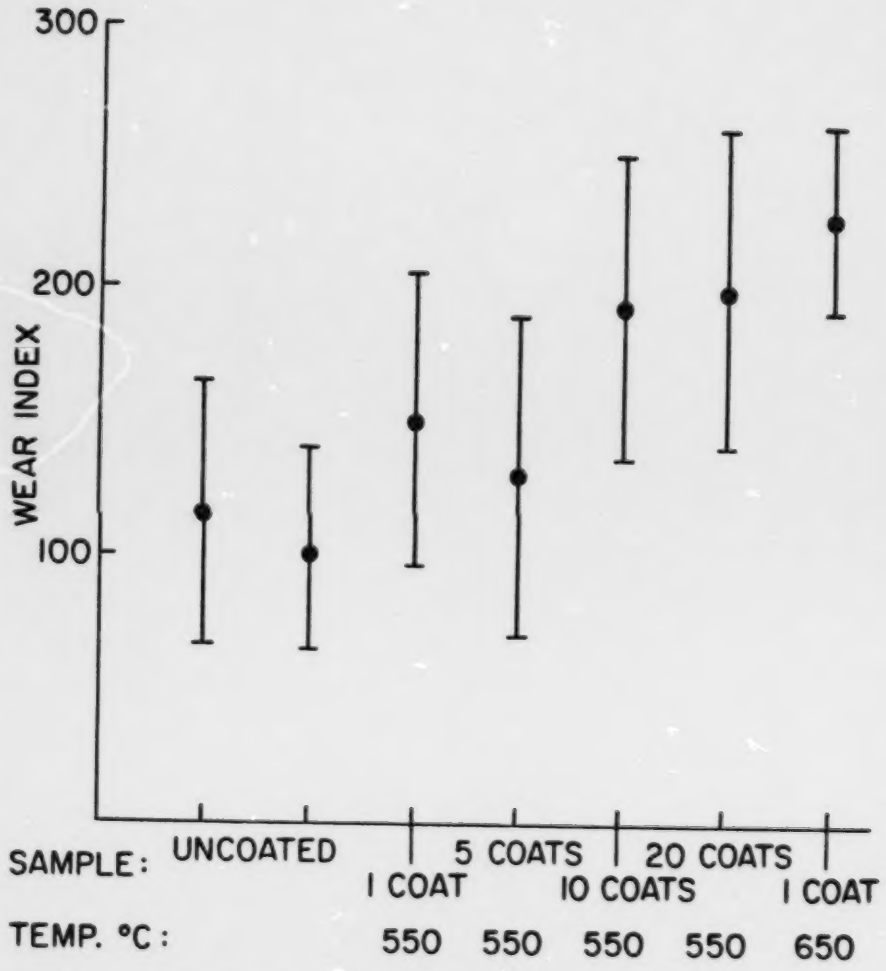


Fig. 7 ABRASION RESISTANCE OF $ZrO_2$ COATED WINDOW GLASS SAMPLES.



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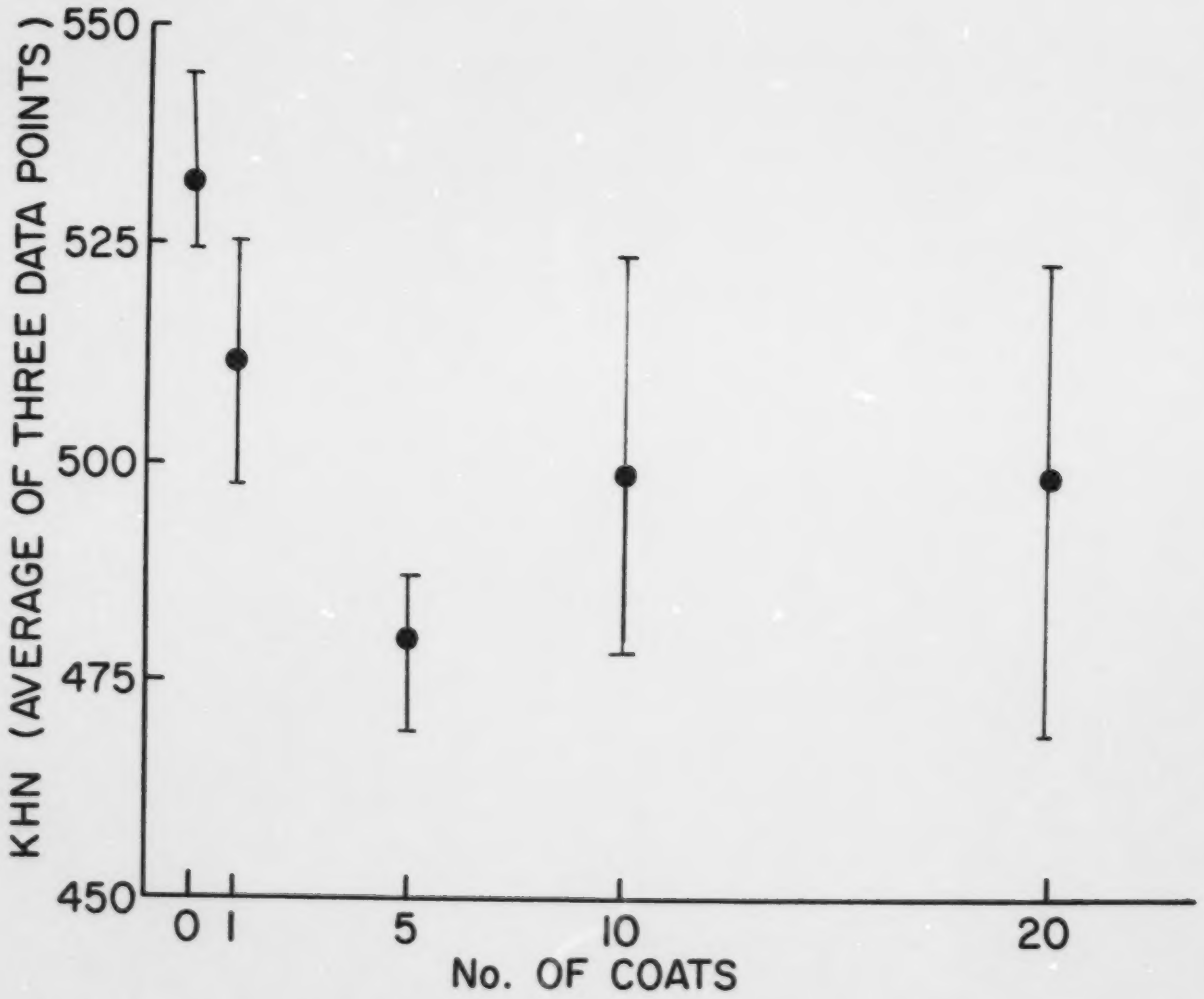


Fig. 8 MICROHARDNESS OF SELECTED GLASS SAMPLES. (100G LOAD)



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These results were consistent with the abrasion resistance data as the $ZrO_2$ films decreased the abrasion resistance of soda-lime glass.

5.1.3.4 Thickness Measurement

(i) Sample Preparation

$ZrO_2$ coated glass samples were prepared for thickness measurements using the Sloan M-100 Angstrometer available at ORF. The thickness range that can be measured with this apparatus if from 250A to 1u. The coating must be deposited so that the edges between the coated and uncoated areas are uniform and clearly defined as shown in Fig. 9.

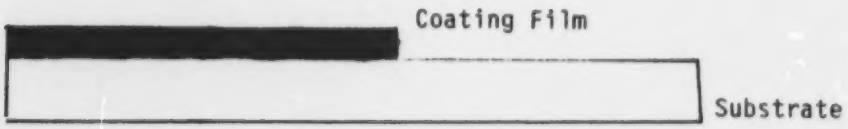


Fig. 9: Suitable Coating for Thickness Measurement

Several techniques were applied in order to achieve the coating as specified in Fig. 9. The uncoated areas were covered with the collowing materials.

- High temperature tapes
- Aluminum foil
- Glass Shield
- Metal Shield
- Graphite spray

The most successful application was the use of graphite spray on the uncoated areas. Graphite films were later removed after the coating operation. This technique provided the most suitable samples for thickness measurements.

(ii) Thickness Measurement of $ZrO_2$ Films

The average thickness of $ZrO_2$ films on glass samples (single coat, 5-second spray) was about 0.1u. As the number of coatings increased, the accurate thickness values were difficult to obtain due to the undefined distinction between the coated and uncoated edge areas. This occured because the protective graphite layer deteriorated during the spraying process. For a $ZrO_2$ film of about 10 coats (5 second spray per coat) the estimated thickness was about 1.2u (Table 2).

Coating thickness was also measured by the SEM cross-section technique. The coating thickness of a sample with 10 coats was about .4u as compared to 1.2u for the Angstrometer technique. This indicated the non-uniformity in thickness of the film. For a sample with 20 coats, the film thickness by the SEM technique was 1.6u.

TABLE 2 Film Thickness

| Sample No. | No. of Coats | Spray time (sec) | Temperature ($^oC$) | Estimated Thickness (A) | (u) | By SEM (μ) |
|---|---|---|---|---|---|---|
| 552 | 1 | 5 | 550 | 1000 | .1 | - |
| 555 | 2 | 5 | 550 | 5000 | .5 | - |
| 559 | 3 | 5 | 550 | 4000 | .4 | - |
| 561 | 5 | 5 | 550 | 2000 | .2 | .2 |
| 563 | 10 | 5 | 550 | 12000 | 1.2 | .4 |
| 607 | 20 | 5 | 550 | - | - | 1.6 |

Details of the thickness measurement are presented in Appendix E.

5.1.3.5 Optical Properties

(i) Experimental Techniques

The reflectance and transmittance of $ZrO_2$ films were measured to determine the potential use for the film in optical applications.



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The infrared reflectance measurements were performed using a Perkin-Elmer 621 Spectrophotometer (University of Toronto, Department of Electrical Engineering) equiped with two specular reflectance accessories. The sample was mounted in one accessory and an aluminum mirror in the other. The angle of incidence was $13^{o}$. The 100% line was obtained by replacing the sample with an aluminum mirror.

The visible transmittance was obtained by using a Perkin-Elmer 450 Spectrophotometer (University of Toronto). The sample was mounted in the sample beam; the reflectance beam was left unobstructed (an uncoated substrate can be placed in the reference beam if required). The 100% line was obtained by removing the sample from the beam.

The optical transmittance in the visible region varied little for coating thicknesses between 1 and 10 coats. The percentage optical transmittance of these coatings were in the 80% range. As the coating thickness increased to about 20 coats, or 1.5$\mu$, the percentage transmittance was reduced to about 50% (Fig. 10).

The reflectance characteristic in the infrared wavelength region of the glass was improved by the $ZrO_2$ film even though the percentage reflectance was low in most of the infrared region (Fig. 11).

5.1.4 Properties of $ZrO_2$ Films on Aluminum Substrates

$ZrO_2$ films deposited on aluminum substrates were evaluated to determine the film structure and composition as well as to identify their useful properties for industrial applications.

5.1.4.1 Structure and Composition of $ZrO_2$ Films

Coated and uncoated aluminum samples were prepared for x-ray analysis. The x-ray spectra showed zirconia peaks for samples with 10 and 20 coats (Fig. 12). These peaks were attributed to the tetragonal/cubic structure. The x-ray spectra for $ZrO_2$ coatings deposited on aluminum and glass substrates were identical.



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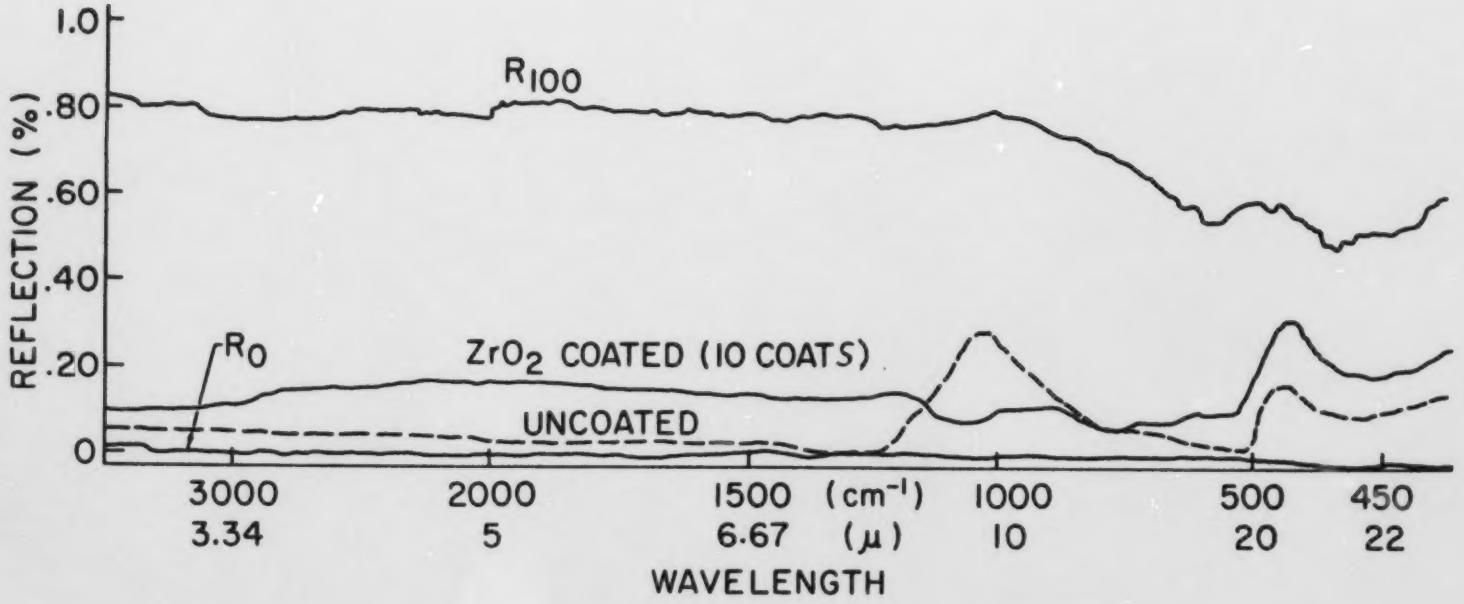


Fig. 10 REFLECTION OF $ZrO_2$ COATED GLASS SAMPLES.



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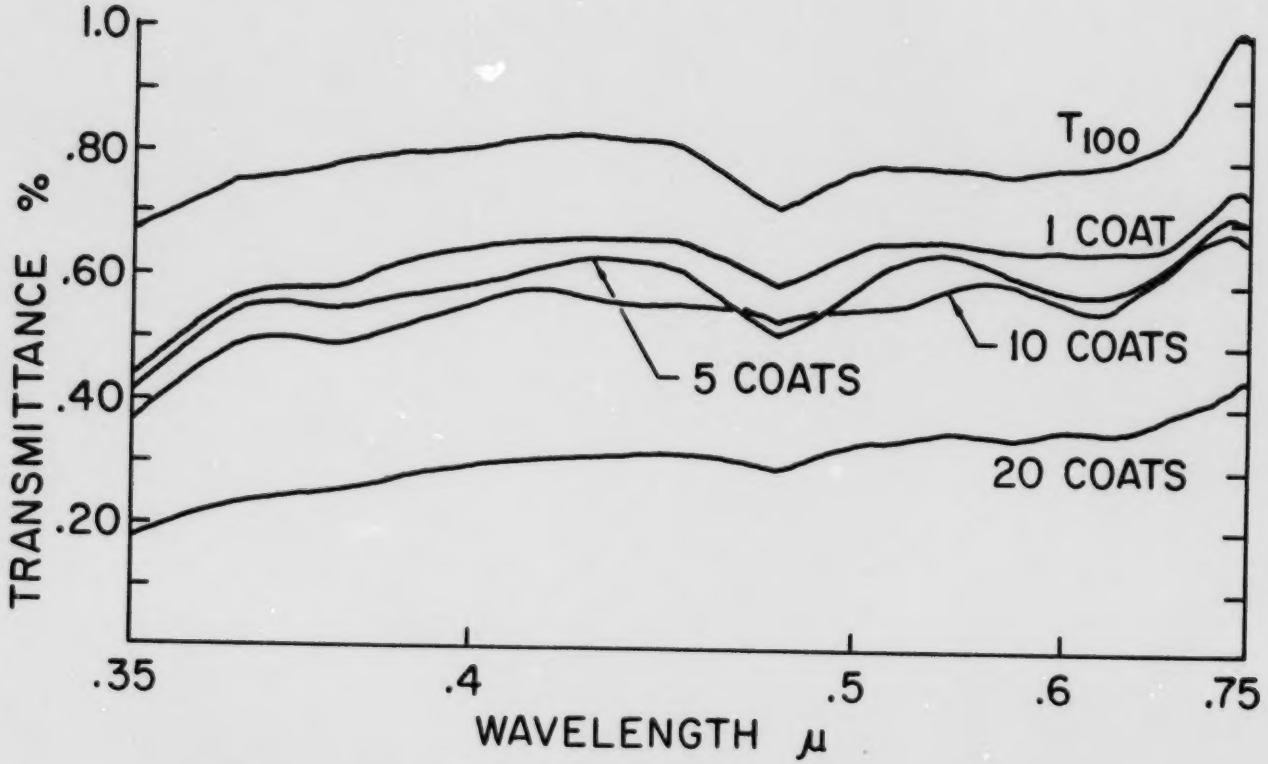


Fig. II TRANSMITTANCE OF $ZrO_2$ FILMS.



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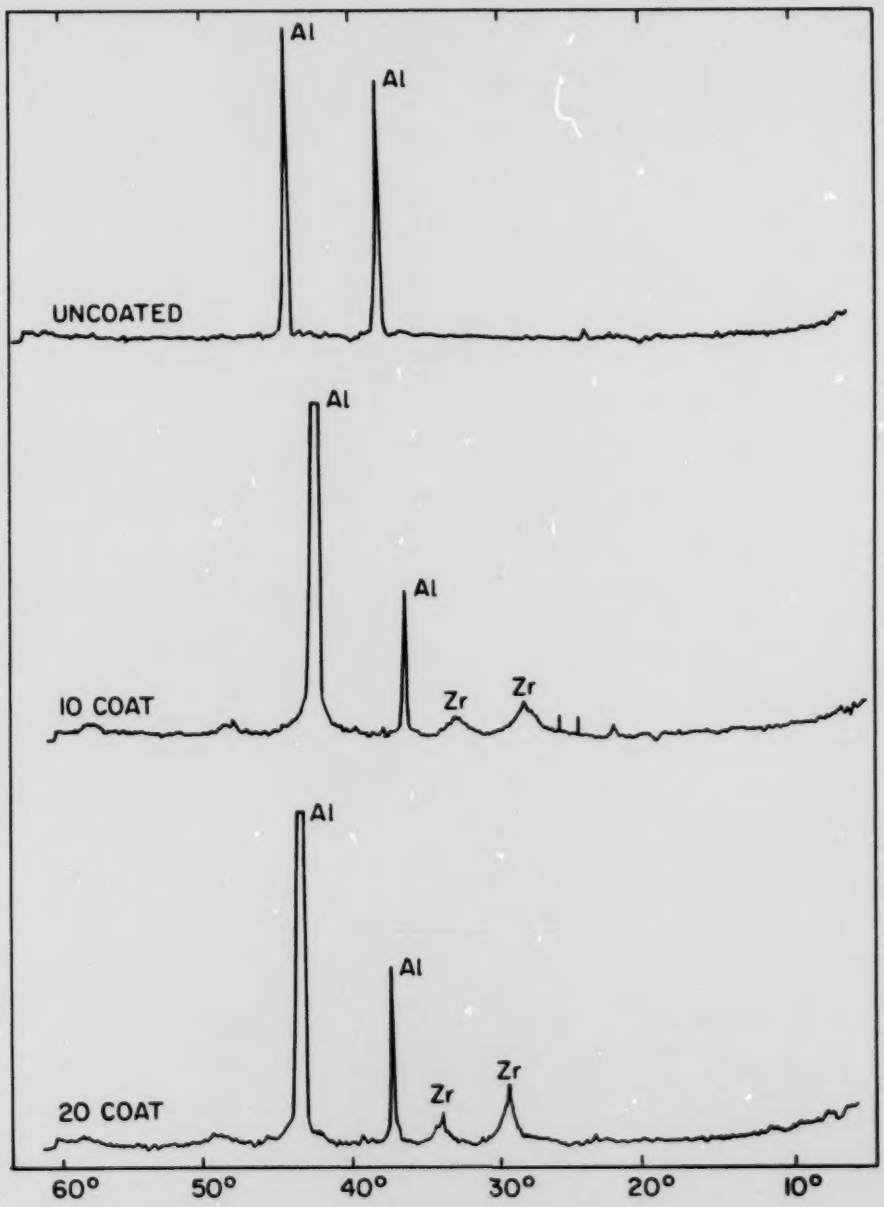
Figure 12 X-RAY ANALYSIS SPECTRA OF COATED & UNCOATED ALUMINUM SAMPLES.



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Energy dispersive x-ray analysis (EDXA) indicated that the film surface consisted of about 17% Zr and 40% Al. The aluminum fraction was from the substrate material (Table 3). An EDXA-spectrum of a sample with 20 $ZrO_2$ coats showed strong Al and Zr peaks in the x-ray energy range of 0 to 20 KeV (Fig. 13).

According to the scanning electron micrographs (SEM) shown in Fig. 14, the $ZrO_2$ on aluminum film was dense and had an adherent micropoly-crystalline structure with a grain size of about 0.5μ in diameter.

5.1.4.2 Abrasion and Hardness Values

The hardness of the $ZrO_2$ films on aluminum substrates were measured using a miniload (10g) microhardness tester equiped with a Knoop indentor. Three indentation points were measured for each sample. The hardness results for these samples showed that the $ZrO_2$ film lowered the hardness value of the aluminum substrate (Fig. 15).

The abrasion resistance of aluminum substrates were significantly improved by the presence of $ZrO_2$ films. Abrasion data are summarized in Appendix F, Table F1. These results were evaluated and analyzed using Student's t-test. The analysis data showed that the wear index of the coated sample is lower than the wear index of the uncoated specimen ($\bar{X}$ coated $< \bar{X}$ uncoated) with 99% of confidence (Table F2, Appendix F).

The mean wear indices are plotted in Fig. 16. As can be observed the abrasion resistance of $ZrO_2$ coated aluminum samples (1 to 20 coats) was about 25% better than that of the uncoated aluminum. This is promising since $ZrO_2$ is also used for high temperature protection. $ZrO_2$ films deposited by spray pyrolysis could be applied to improve the abrasion resistance as well as raise the working temperature of aluminum materials.

As the coating thickness increased (40 coats $\backsim$ 2μ), the abrasion resistance of the coated specimens decreased substantially. This factor will limit the maximum thickness of the film if improvement of the abrasion resistance of an aluminum substrate is the objective.



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TABLE 3

ED X-Ray Analysis of $ZrO_2$ Film on Aluminum

SPECTRUM 517DN-ALGL FEB. 3. 1984

| | |
|---|---|
| ACCELERATING VOLTAGE | 30.0 KEV |
| INCIDENCE ANGLE | 60.0 DEGREES |
| EFFECTIVE TAKE-OFF ANGLE | 54.0 DEGREES |

STANDARDLESS EDS ANALYSIS
(ZAF CORRECTIONS VIA MAGIC V)

| ELEMENT & LINE | K-RATIO | WEIGHT PERCENT | PRECISION 2 SIGMA | OXIDE FORMULA | OXIDE PERCENT | NO. OF CATIONS IN FORMULA |
|---|---|---|---|---|---|---|
| AL KA | 0.8032 | 40.41 | 0.22 | AL2O3 | 76.35 | 1.1392 |
| FE KA | 0.0085 | 0.39 | 0.04 | FEO | 0.50 | 0.0053 |
| ZR LA | 0.1882 | 17.14 | 0.39 | ZRO2 | 23.15 | 0.1429 |
| O * | | 42.06 | | | | |
| TOTAL | | | | | 100.00 | 1.2875 |

NUMBER OF CATIONS CALCULATED ON BASIS OF 2 OXYGEN ATOMS.

* DETERMINED BY STOICHIOMETRY



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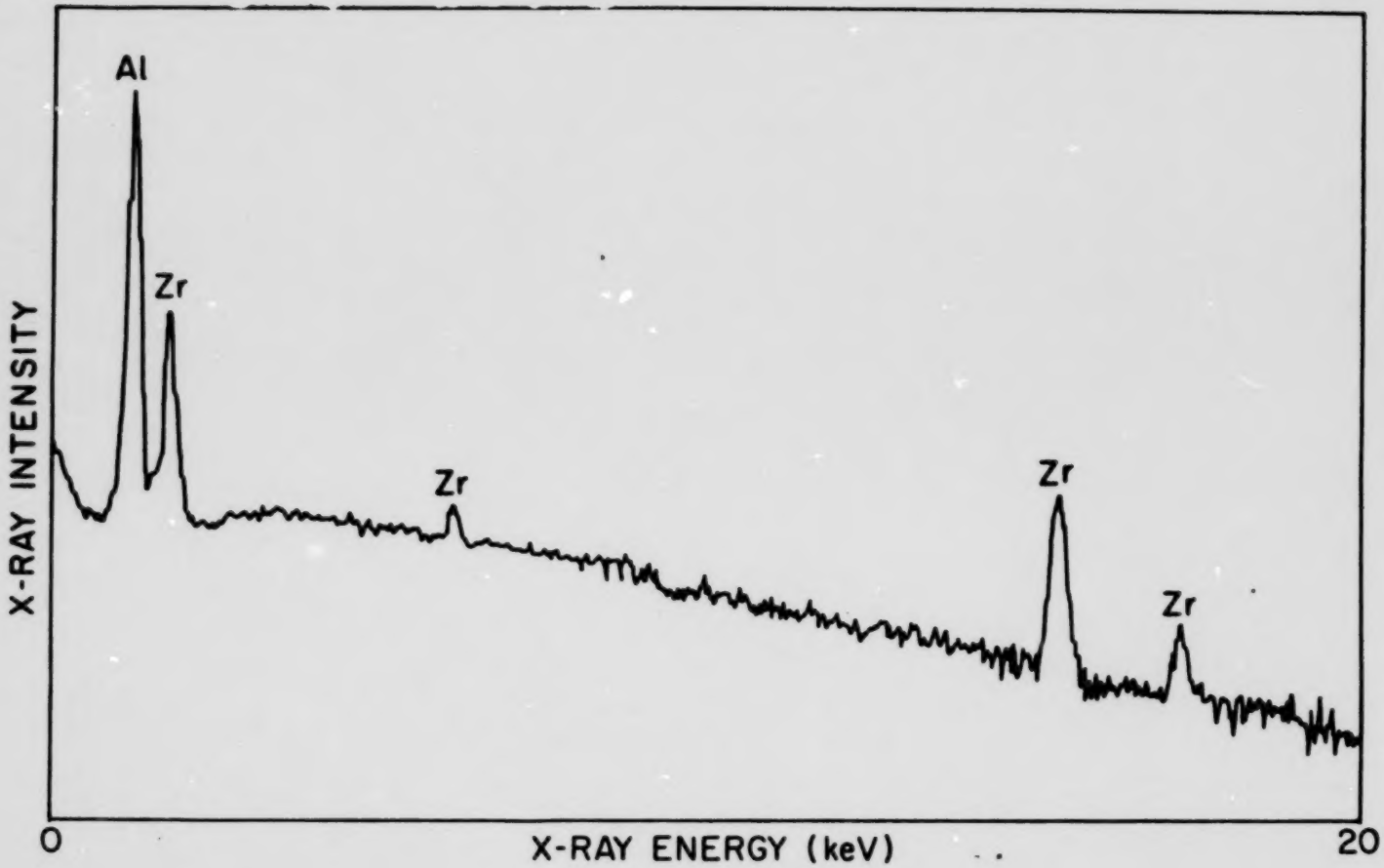


Figure 13 EDX-Ray Analysis of $ZrO_2$ Film on Aluminum (#286 - 20 coats)



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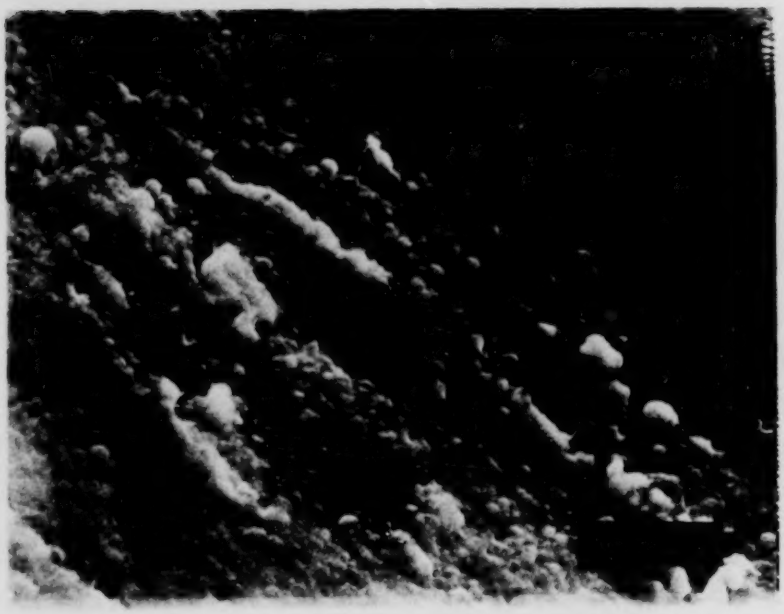
Figure 14 $ZrO_2$ Film on Aluminum
(#286 - 20 coats)



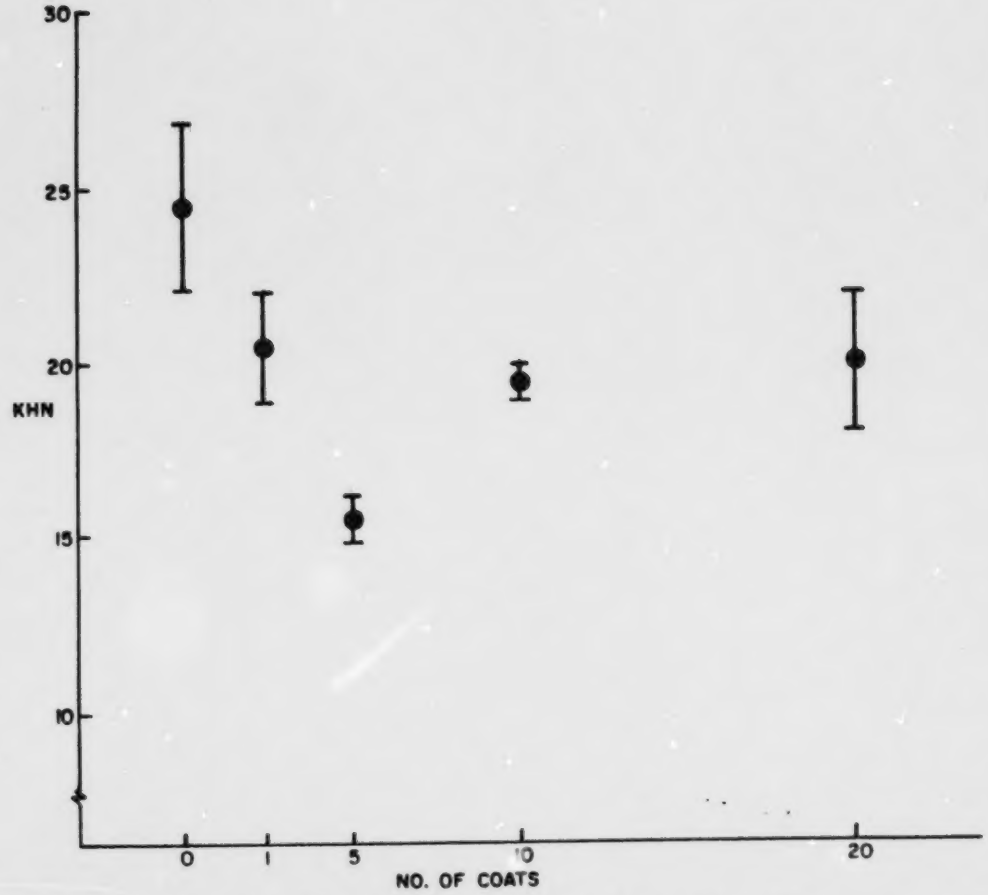



Figure 15 Microhardness of Selected Aluminum Samples (10g Load)

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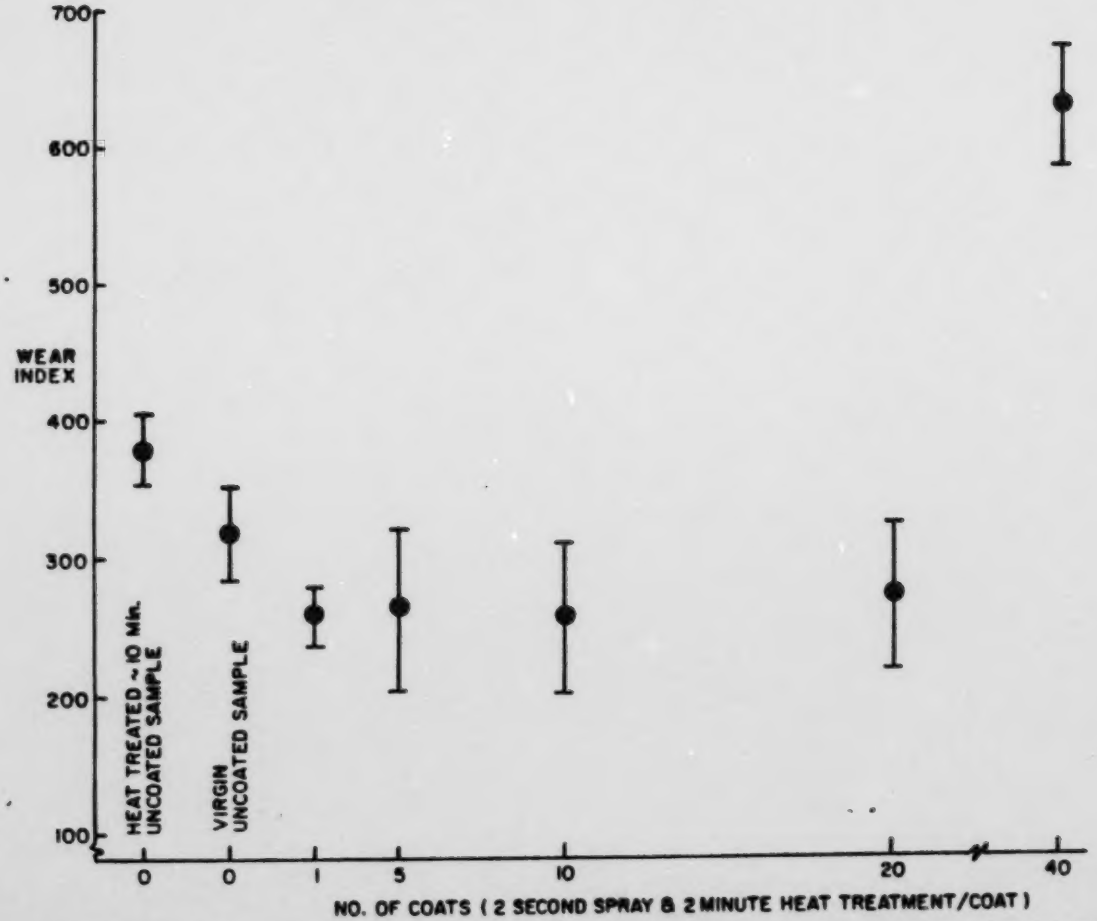
Figure 16 Abrasion Resistance of Coated and Uncoated Aluminum Samples



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5.1.5 Other Substrates - High Temperature Oxidation Resistance

Two series of heat treatment experiments were carried out to evaluate the heat resistance of $ZrO_2$ films.

The first test included the evaluation of stainless steel 310 and 304 coated with $ZrO_2$ film (Table G1, Appendix G). The heat treatment program for this experiment was 1000°C for 24 hours and 800°C for 5 hours. At high temperature and long soak time (1000°C, 24 hours), no significant differences were observed between coated and uncoated samples (Figs. G1 and G2, Appendix G). However, at lower temperature and shorter soak times (800°C, 5 hours), there is a distinction in colour between the coated and uncoated samples, especially for samples prepared at 500°C, single coat (Figs. G3 and G4, Appendix G).

The second test series involved nickel plated mild steel, carbon steel, TiC coated carbon steel, ss 304. All these substrates were coated with $ZrO_2$ and were subjected to a heat treatment experiment which included heating the samples to 800°C and soaking at this temperature for 1 hour. The results of the heat treatment test are shown in Table G2, Appendix G.

It was found that nickel plated mild steel and ss 304 were not affected by the heat treatment schedule. On the other hand, for carbon steel, the impact of the test program was quite severe; all carbon steel samples - coated and uncoated - were completely destroyed.

The most promising result involved TiC coated carbon steel. The presence of zirconia films improved the high temperature oxidation resistance of TiC material. The $ZrO_2$ coated samples remained unchanged (Fig. 17), while in the case of uncoated specimens, layers of TiC and steel flaked off (Fig. 18).

This is an interesting property of the $ZrO_2$ film prepared by spray pyrolysis. The $ZrO_2$ film can be used to enhance the service life of TiC coated substrates in a high temperature environment.



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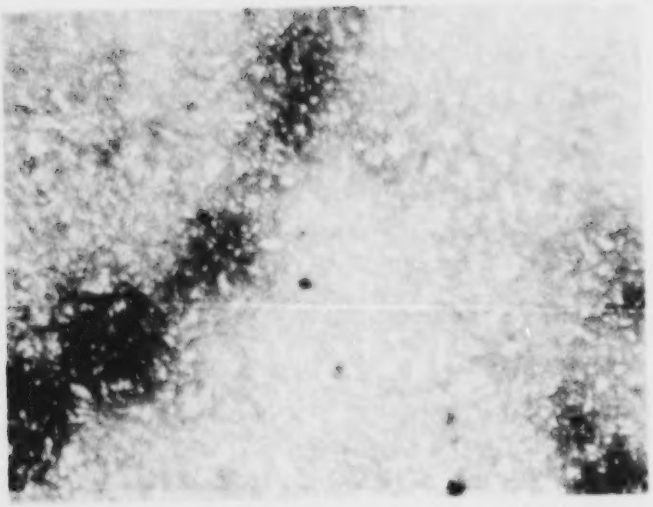

Figure 17: $ZrO_2$ Film on TiC Coated Carbon Steel - Heat treated at 800°C, 1 hour, x370

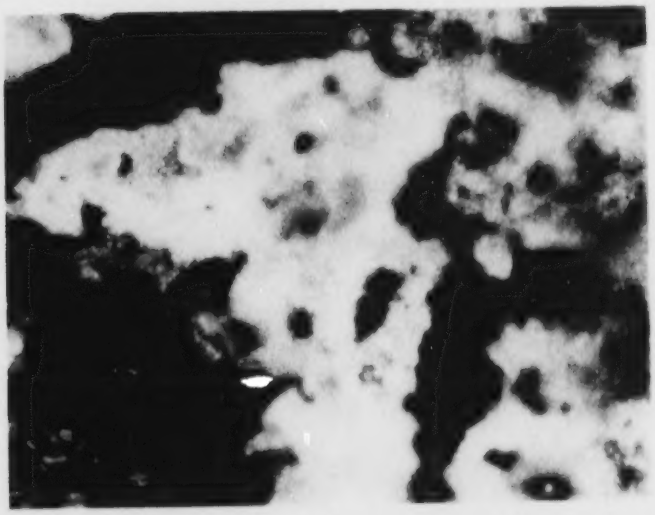

Figure 18: Uncoated TiC Coated Carbon Steel Heat treated at 800°C, 1 hour, x370.

## 5.2 $Al_2O_3/ZrO_2$ Mixed Films

A mixed solution of butyl zirconate and aluminum sec-butoxide was prepared for spray pyrolysis of $Al_2O_3/ZrO_2$ films. The concentrations of aluminum sec-butoxide in butyl zirconate were 20 and 50 percent by volume. No solvent was used for this mixed solution.

Window glass samples were sprayed with this solution at a furnace temperature of 550°C (Table H1, Appendix H). Transparent thin films with excellent adhesion were obtained. There was a little difference in appearance between the $ZrO_2$ and $ZrO/Al_2O_3$ mixed films. The mixed $Al_2O_3/ZrO_2$ film covered larger surface areas and had a cloudy white colour at high aluminum sec-butoxide concentrations.

X-ray analysis of these coatings (Fig. 19) showed no peaks in the angular range of $2\theta = 6$ to 62° (nickel filtered $CuK_\alpha$ radiation).

## 5.3 $Al_2O_3$ Films

### 5.3.1 Solution Evaluation

Based on the experimental results of Phase I of the program, the most promising solutions were selected for alumina ($Al_2O_3$) coating trials. The candidate materials were aluminum sec-butoxide and aluminum isopropoxide. Solvents were required since aluminum isopropoxide was solid and aluminum sec-butoxide solution oxidized and gelled on exposure to the atmosphere. Preliminary evaluations of several organic solvents indicated that toluene was most suitable as an organic solvent and aluminum sec-butoxide was the better precursor material.

### 5.3.2 Substrate Evaluation

The aluminum sec-butoxide solution $Al(C_4H_9O)_3$ (ICN Pharmaceuticals Inc. NY, USA) was added to toluene at a concentration of about 70% by volume. The substrates evaluated were soda-lime glass, carbon steel, nickel plated mild steel, TiC coated steel, aluminum, 304 ss. As shown in Table H2, Appendix H, except for some difficulties with carbon steel mainly due to a problem with the spray system, other substrates were successfully coated with amorphous $Al_2O_3$ films. However, because of time restrictions, the property evaluation of the $Al_2O_3$ coatings on various substrates could not be pursued further.

000037 ORF

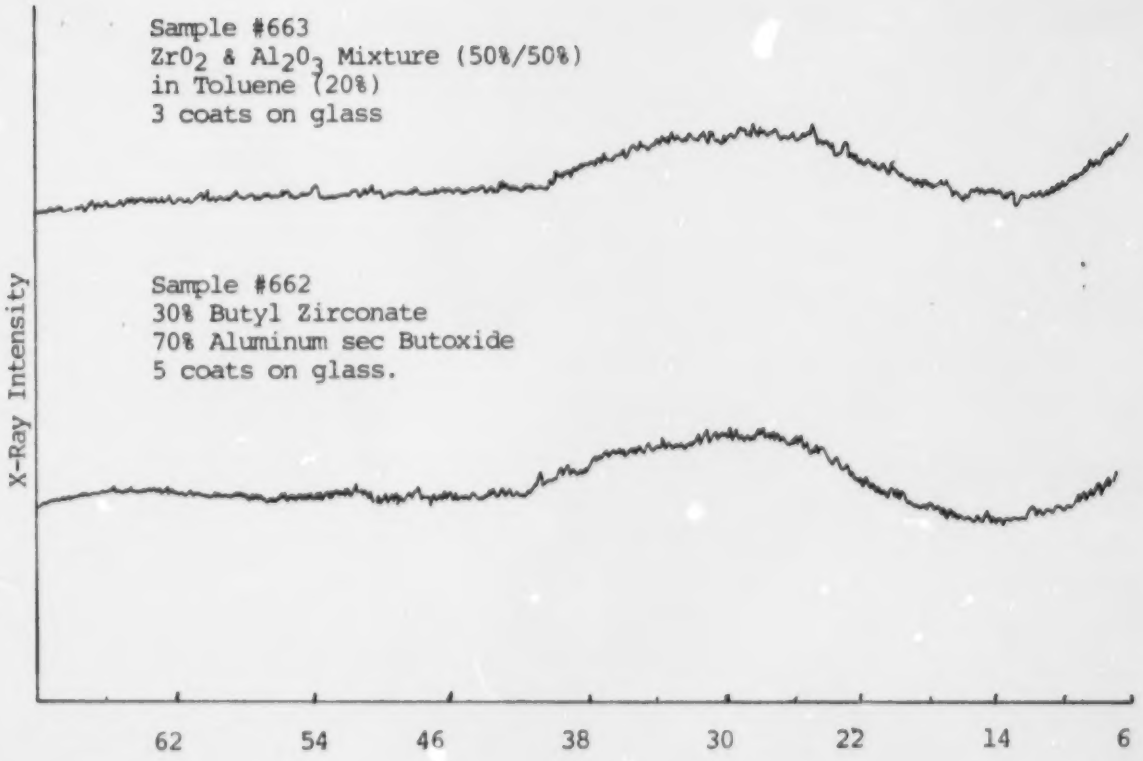


Fig. 19
X-Ray Analysis of $Al_2O_3/ZrO_2$ Film on
Window Glass



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### 5.3.3 Structure and Composition of $Al_2O_3$ Films

Glass samples coated with $Al_2O_3$ were cut and prepared for optical microscopy, x-ray analysis and SEM and EDXA. The x-ray diffraction spectrum showed no presence of crystalline phases (Fig. 20). Energy dispersive analysis (EDXA) spectra (Fig. 21 and Table 4) indicated the presence of aluminum on the glass surface. The concentration of aluminum oxide on the glass substrate was estimated to be about 53 percent (Table 4). The peaks of Si, Na and Ca from the soda-lime glass substrate were also present due to the scattering effect.

Electron micrographs of the aluminum film showed that the film was dense and free of microcracks. It had a micropolycrystalline structure with a grain size diameter of about 4μ (Fig. 22(a) and (b)). An optical micrograph of an $Al_2O_3$ film on glass is shown in Fig. 23.

This glassy film has the potential for applications in the fabrication of semiconductor devices which requires the passivation of the semiconductor surface. $Al_2O_3$ films are desirable since they can replace $SiO_2$ films which exhibit instabilities in the presence of impurities and Na ions.

### 5.4 Industrial Potential of $ZrO_2$ Films by Spray Pyrolysis

The potential applications of $ZrO_2$ films by spray pyrolysis were evaluated. The present uses of $ZrO_2$ films and their properties were compiled and analyzed. The results are given in Appendix I.



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## 6. CONCLUSIONS AND RECOMMENDATIONS

A process for the deposition of thin ceramic films ($ZrO_2$, $Al_2O_3$, $ZrO_2$-$Al_2O_3$ mixed films) using spray pyrolysis of alkoxide precusor solutions was successfully developed under this program. The coating substrate onto which these coatings were deposited were mainly soda lime glass but other substrates such as aluminum, carbon steel, stainless steel, TiC coated carbon steel and nickel plated mild steel were also used.

The $ZrO_2$ coatings were polycrystalline (tetragonal or cubic). They were transparent and showed good adherence. Their thickness increased with the number of consecutive sprays. A $ZrO_2$ coating after 20 cycles was found to have a thickness of 1.6 u. $Al_2O_3$, $ZrO_2$-$Al_2O_3$ and $TiO_2$ coatings appeared to have similar characteristics.

An extensive investigation of the properties of $ZrO_2$ coated substrates showed that these coatings did improve the high temperature oxidation resistance of TiC coated steel. The coating was found to improve the abrasion resistance of aluminum but not of soda-lime glass substrates.

The $ZrO_2$ coatings were also found to be transparent for thicknesses up to 10 coats on soda-lime glass substrates. To utilize the full potential of the coatings produced under this program further research would be required. The following areas, in particular, deserve attention:

(a) Basic research into the transformations of the various phases in thin $ZrO_2$ films prepared by spray pyrolysis and its effect on coating properties. The effect of dopants with stabilizing properties ($Y_2O_3$, CaO) could be of interest.

(b) A more extensive optimization of the $Al_2O_3$ coating for abrasion resistance improvement and corrosion protection. The use of thin amorphous $Al_2O_3$ films for dielectric applications in integrated circuits should also be investigated.

(c) The ease with which several oxide coatings have been deposited from alkoxide precursors using the spray pyrolysis technique suggests that this technique may be widely applicable to a large number of oxide coatings (mixed as well as single) on a variety of substrates. Possible application would be in the field of solar technology (solar absorbers, anti-reflecting coatings),etc.

## 7. ACKNOWLEDGEMENTS

The authors would like to thank W. Smeaton for preparation and testing of samples.

D. Nguyen

M. van Roode

Materials Division
Glass and Ceramics Centre

Fig. 20 X-Ray Analysis of $Al_2O_3$ Film on Glass

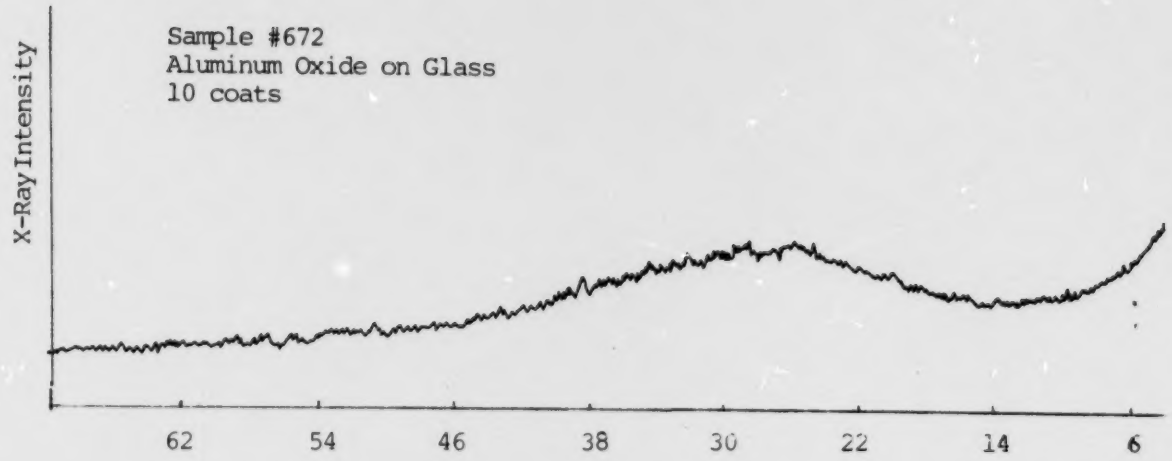


Fig. 21 EDXA Spectra of $Al_2O_3$ Film on Glass

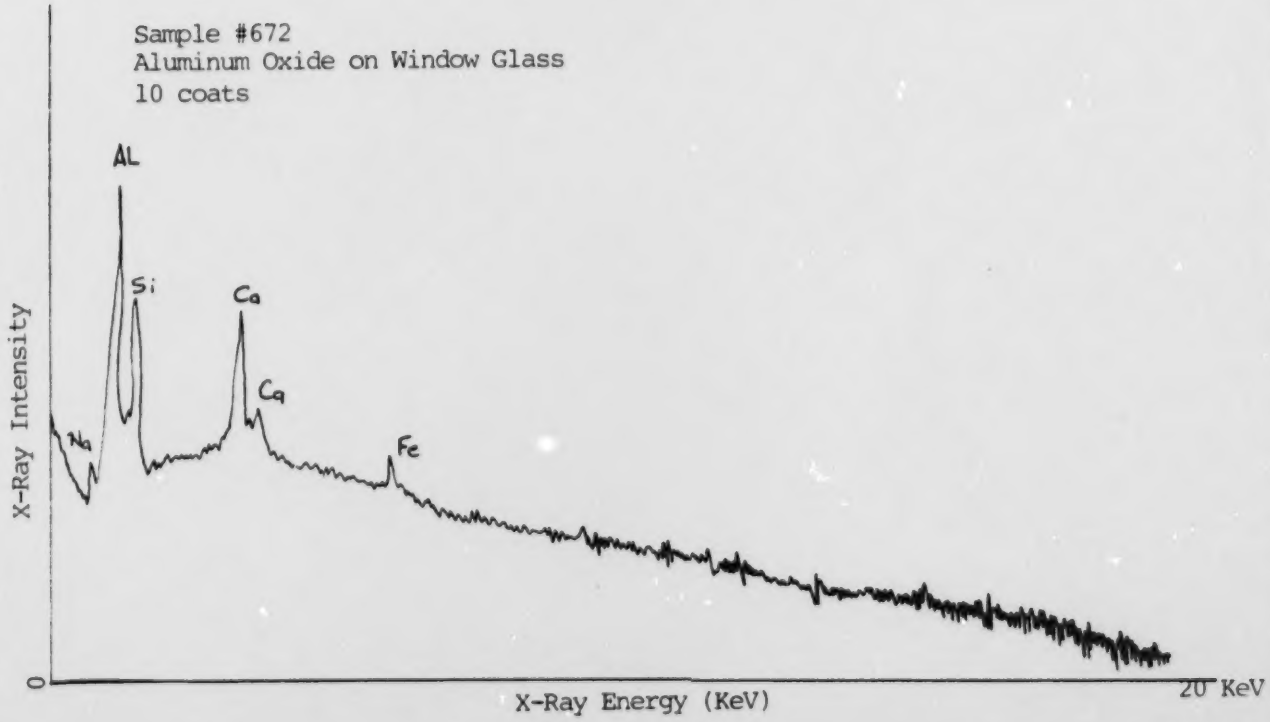




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TABLE 4

EDX-ray analysis of Alumina Film on Glass

SPECTRUM 517DN-ALGL FEB. 3. 1984

| | |
|---|---|
| ACCELERATING VOLTAGE | 30.0 KEV |
| INCIDENCE ANGLE | 60.0 DEGREES |
| EFFECTIVE TAKE-OFF ANGLE | 54.0 DEGREES |

STANDARDLESS EDS ANALYSIS
(ZAF CORRECTIONS VIA MAGIC V)

| ELEMENT & LINE | K-RATIO | WEIGHT PERCENT | PRECISION 2 SIGMA | OXIDE FORMULA | OXIDE PERCENT | NO. OF CATIONS IN FORMULA |
|---|---|---|---|---|---|---|
| NA KA | 0.0010 | 0.10 | 0.01 | NA2O | 0.13 | 0.0029 |
| AL KA | 0.6062 | 28.30 | 0.29 | AL2O3 | 53.47 | 0.7323 |
| SI KA | 0.1194 | 13.92 | 0.36 | SIO2 | 29.78 | 0.3461 |
| P KA | 0.0019 | 0.23 | 0.05 | P2O5 | 0.52 | 0.0051 |
| S KA | 0.0025 | 0.21 | 0.04 | SO3 | 0.54 | 0.0047 |
| CL KA | 0.0014 | 0.09 | 0.03 | CL | 0.09 | 0.0000 |
| CA KA | 0.2010 | 8.46 | 0.22 | CAO | 11.84 | 0.1473 |
| FE KA | 0.0176 | 0.62 | 0.08 | FEO | 0.80 | 0.0077 |
| SN LA | 0.0491 | 2.23 | 0.19 | SNO2 | 2.83 | 0.0131 |
| O * | | 45.84 | | | | |
| TOTAL | | | | | 100.00 | 1.2592 |

NUMBER OF CATIONS CALCULATED ON BASIS OF 2 OXYGEN ATOMS.

* DETERMINED BY STOICHIOMETRY



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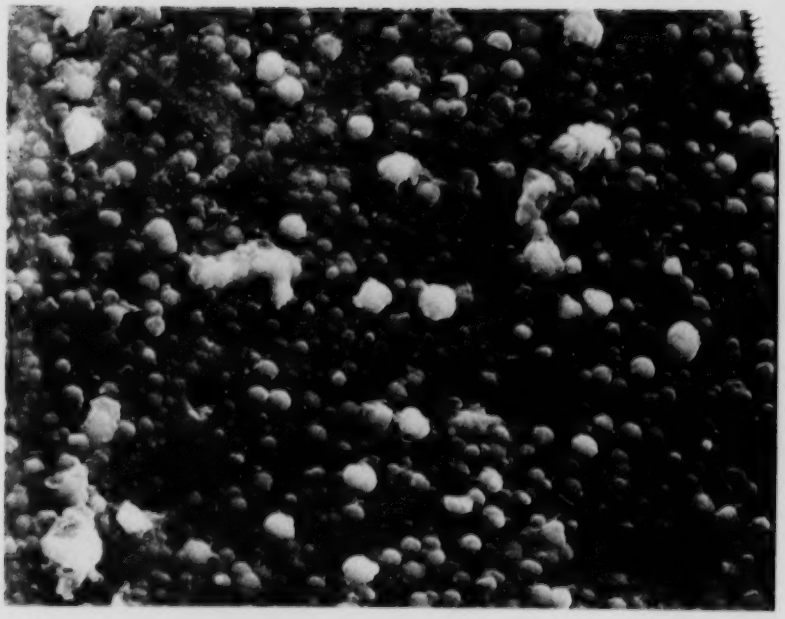
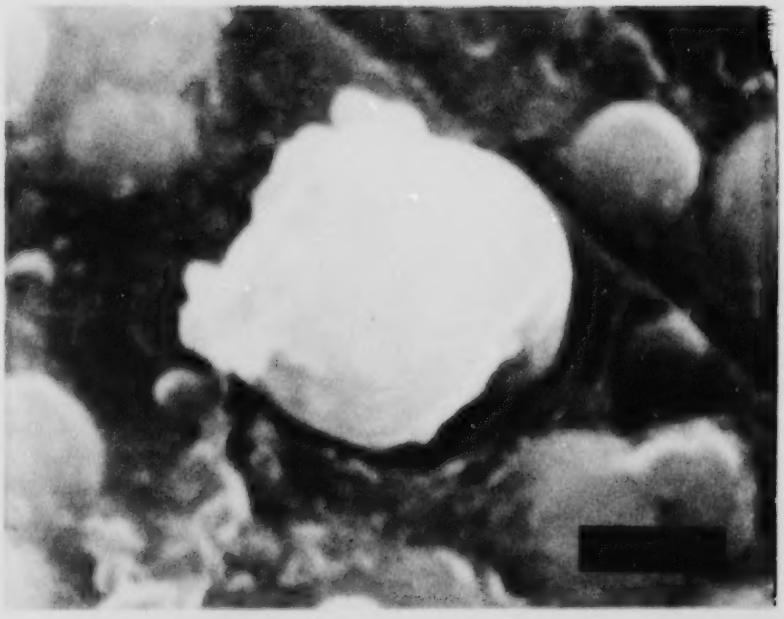
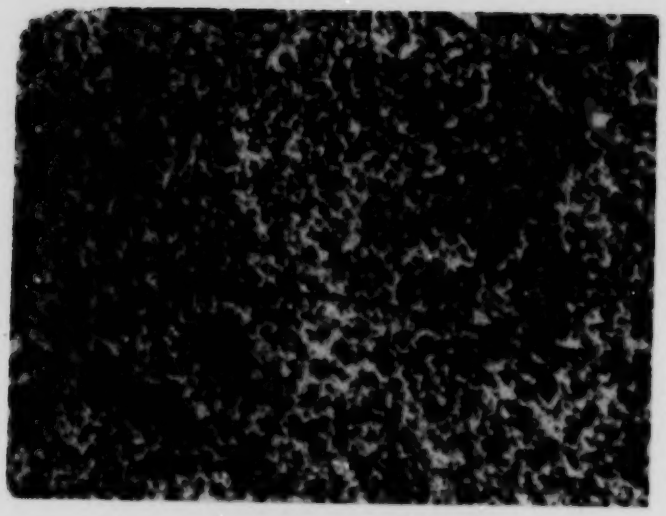


(a)



(b)

Fig. 22 Alumina Films on Window Glass - 10 Coats, #672



Optical micrograph of

Fig. 23 $Al_2O_3$ Coating on Window Glass, Temperature $550^{o}$ - 10 coats, #672, x185

## APPENDIX A

Computer Program for the Control System of the
Spray Pyrolysis Facility and Data on the
Parameter Modifications



ORF

```
PAGE 001  SPPROG  .SA:1

00010  BYTE PTMBAS ADDR $EF20,PTMBAS1 ADDR $EF21,ADLOW ADDR $ED39
00020  INTEGER DUMMY2,DUMMY5,NCYCLES,I,J,K,N,AD12N,COUNTER,INDICATER
00025  INTEGER M,KK
00030  BYTE DUMMY1,DUMMY3,DUMMY4
00040  INTEGER COUNT ADDR $EF26,AD12_0 ADDR $ED40,AD12_4 ADDR $ED48
00050  INTEGER PIAASTAT ADDR $ED60,AD16 ADDR $ED3A
00060  BYTE PIAA ADDR $ED60,PIAAC ADDR $ED61,PIAB ADDR $ED62,PIABC ADDR $ED63
00070  REM *SD(1)=counter,(I,2)=furntemp,(I,3)=samtemp,(I,4)=piaastat,*
00080  REM *SD(5)=spraypress*
00090  INTEGER SD(6)
00100  DIM ONN(10),OFF(10)
00110 INPUT "print data (Y or N ?)", Q$
00120  IF Q$# CHR$($59) AND Q$# CHR$($4E) THEN  GOTO 110
00130  IF Q$# CHR$($59) THEN  GOTO 150
00140 INPUT "sample I.D.", FNAME
00150  INPUT "enter the furnace duration (sec)",FTIME
00160  INPUT "enter 1-cooling period,2-spray temp,0-immed. spray",CFLAG
00170  IF CFLAG#1 AND CFLAG#2 THEN  GOTO 230
00180  IF CFLAG#1 THEN  GOTO 210
00190  INPUT "spec. cooling per.(sec)",CTIME
00200  GOTO 230
00210  INPUT "spec. spray temp.(C)",SPTEMP
00220  GOSUB 2420
00230  PRINT "ENTER THE ON & OFF SPRAY SEQ.,& THEN THE # OF CYCLES"
00240  J=0
00250  PRINT " "
00260  J=J+1
00270  INPUT "enter the on period (0 to quit)",ONN(J)
00280  IF ONN(J)=0 THEN  GOTO 320
00290  INPUT "enter the off period (0 to quit)",OFF(J)
00300  IF OFF(J)=0 THEN  GOTO 320
00310  GO  TO 260
00320  INPUT "enter the number of cycles",NCYCLES
00322  NCYCLES = NCYCLES+1
00325 INPUT "annealing period after the spray cycle",CTIME2
00330  REM *init pia*
00340  GOSUB 930
00350  COUNTER=0
00370  REM *continuously monitor timer*
00380  ON  NMI  THEN  GOSUB 1080
00390  REM *init. ptm*
00400  GOSUB 1010
00410  I=0
00415 FOR K=1 TO NCYCLES
00417 IF K=NCYCLES THEN FTIME=CTIME2
00418 IF CTIME2=0 THEN GOTO 820
00420  REM *store furnace data*
00430  GOSUB 2910
00440  REM *open lids*
00450  PIAB[2]=0
00460  REM *check lids*
00470  GOSUB 1170
00480  REM *lower sample*
00490  PIAB[0]=0
00500  REM *check sample*
00510  GOSUB 1450
00520  REM *close lids*
00530  PIAB[2]=1
```



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```
00540  REM *check lids*
00550  GOSUB 1310
00560  REM *furnace duration seq.*
00570  GOSUB 2140
00580  REM *open lids*
00590  PIAB[2]=0
00600  REM *check lids*
00610  GOSUB 1170
00620  REM *lift sample*
00630  PIAB[0]=1
00640  REM *check sample*
00650  GOSUB 1590
00660  REM *close lids*
00670  PIAB[2]=1
00680  REM *check lids*
00690  GOSUB 1310
00700  REM *cooling period routine*
00705 IF K = NCYCLES THEN GOTO 820
00710  IF CFLAG$1 AND CFLAG$2 THEN  GOTO 750
00720  INCREM=10
00730  IF CFLAG=1 THEN  GOSUB 2280
00740  IF CFLAG=2 THEN  GOSUB 2620
00750  REM *activate spray cycle*
00760  GOSUB 1740
00766 NEXT K
00820 PTMBAS=$3
00910  STOP
00920  REM ---------
00930  REM pia init.
00950  PIAA=$0
00960  PIAAC=$4
00970  PIAB=$FF
00980  PIABC=$4
00990  PIAB=$FF
01000  RETURN
01010  REM timer initialization routine
01030  PTMBAS1[0]=0
01040  PTMBAS=$3
01050  COUNT=$30D4
01060  PTMBAS=$43
01070  RETURN
01080  REM timing routine
01100  COUNTER=COUNTER+1
01110  TIME=COUNTER/10
01120  DUMMY1=PTMBAS1
01130  DUMMY2=COUNT
01140  DUMMY3=PIAAC
01150  DUMMY4=PIABC
01160  RETURN
01170  REM lids open check routine
01190  TIME0=TIME
01200  IF PIAA[2]=0 AND PIAA[3]=0 THEN  GOTO 1300
01210  DTIME=TIME-TIME0
01220  IF DTIME<3 THEN  GOTO 1200
01230  GOSUB 1721
01260  PRINT "***CHECK TO SEE IF LIDS ARE OPEN***"
01270  GOSUB 1726
01300  RETURN
```



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```
01310  REM lids close check routine
01330  TIME0=TIME
01340  IF PIAA[0]=0 AND PIAA[1]=0 THEN  GOTO 1440
01350  DTIME=TIME-TIME0
01360  IF DTIME<3 THEN  GOTO 1340
01370  GOSUB 1721
01400  PRINT "***CHECK TO SEE IF LIDS ARE CLOSED***"
01410  GOSUB 1726
01440  RETURN
01450  REM sample down check routine
01470  TIME0=TIME
01480  IF PIAA[5]=0 THEN  GOTO 1580
01490  DTIME=TIME-TIME0
01500  IF DTIME<3 THEN  GOTO 1480
01510  GOSUB 1721
01540  PRINT "***CHECK TO SEE IF SAMPLE IS DOWN***"
01550  GOSUB 1726
01580  RETURN
01590  REM sample up check routine
01610  TIME0=TIME
01620  IF PIAA[4]=0 THEN  GOTO 1720
01630  DTIME=TIME-TIME0
01640  IF DTIME<3 THEN  GOTO 1620
01650  GOSUB 1721
01680  PRINT "***CHECK TO SEE IF SAMPLE IS UP***"
01690  GOSUB 1726
01720  RETURN
01721  REM *BELL*
01722  FOR I=1 TO 5
01723  PRINT  CHR$(7)
01724  NEXT I
01725  RETURN
01726  REM *PAUSE*
01727  PRINT " "
01728  PRINT "PRESS ANY CHARACTER KEY TO COUNTINUE"
01729  PAUSE
01730  RETURN
01740  REM *spray sequence*
01760  J=0
01770  J=J+1
01780  IF ONN(J)=0 THEN  GOTO 2020
01790 REM PIAB[6]=0,PIAB[4]=0,PIAB[2]=1,PIAB[0]=1
01800 PIAB=5
01810  INDICATER=$FFFF
01820  TIME0=TIME
01830  INCREM=.2
01840  GOSUB 2790
01850  DIFF=TIME-TIME0
01860  IF DIFF>=ONN(J) THEN  GOTO 1900
01870  DIFF2=TIME-SETTIME
01880  IF DIFF2>=INCREM THEN  GOTO 1840
01890  GOTO 1850
01900  PIAB[4]=1
01910  PIAB[6]=1
01920  INDICATER=0
01930  IF OFF(J)=0 THEN  GOTO 2020
01940  TIME0=TIME
01950  GOSUB 2790
```



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```
01960  DIFF=TIME-TIME0
01970  IF DIFF>=OFF(J) THEN  GOTO 1770
01980  DIFF2=TIME-SETTIME
01990  IF DIFF2>=INCREM THEN  GOTO 1950
02000  GOTO 1960
02020  RETURN
02030  REM *AD16 temp routine*
02050  ADLOW=CHAN
02060  IF ADLOW[5]=0 THEN  GOTO 2080
02070  GOTO 2060
02080  RETURN
02090  REM *DELAY*
02120  FOR KK=1 TO 2
02125  NEXT KK
02130  RETURN
02140  REM *furnace duration routine*
02160  TIME0=TIME
02170  SETTIME=TIME
02180  REM *store furnace data*
02190  GOSUB 2910
02200  DIFF1=TIME-TIME0
02210  IF DIFF1>=FTIME THEN  GOTO 2250
02220  DIFF2=TIME-SETTIME
02230  IF DIFF2>=10 THEN  GOTO 2170
02240  GOTO 2200
02250  REM *store furnace data*
02260  GOSUB 2910
02270  RETURN
02280  REM *cool for spec. period routine*
02300  TIME0=TIME
02310  SETTIME=TIME
02320  REM *store data*
02330  GOSUB 3030
02340  DIFF1=TIME-TIME0
02350  IF DIFF1>=CTIME THEN  GOTO 2390
02360  DIFF2=TIME-SETTIME
02370  IF DIFF2>=INCREM THEN  GOTO 2310
02380  GOTO 2340
02390  REM *store data*
02400  GOSUB 3030
02410  RETURN
02420  REM *convert sptemp to ad12 reading*
02440  REM *RANGE 0C-1200C (0-2047 AD12)*
02450  REM *DETERM. E (MICROVOLTS) FROM SPTEMP*
02460  DATA 2.5132785E-2,-6.0883423E-8,5.5358209E-13,9.3720918E-18
02470  READ A1,A2,A3,A4
02480  E=0
02490  E=E+100
02500  T=A1*E+A2*E^2+A3*E^3+A4*E^4
02510  IF T>SPTEMP THEN  GOTO 2530
02520  GOTO 2490
02530  E=E-100
02540  T=A1*E+A2*E^2+A3*E^3+A4*E^4
02550  IF T>=SPTEMP THEN  GOTO 2590
02560  E=E+1
02570  GOTO 2540
02580  REM *conv. SPTEMP to an ad12 reading*
02590  SPTEMP=(2047/48828)*E
```

02600 SPTEMP=FIX(SPTEMP)

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```
02600  SPTEMP= FIX(SPTEMP)
02610  RETURN
02620  REM *cooling period (spec. temp) routine*
02640  SETTIME=TIME
02650  REM *store data*
02660  GOSUB 3030
02670  AD12N=AD12_0
02680  GOSUB 2090
02690  STEMP=AD12_0
02700  IF STEMP<=SPTEMP THEN  GOTO 2740
02710  DIFF=TIME-SETTIME
02720  IF DIFF>=INCREM THEN  GOTO 2640
02730  GOTO 2670
02740  REM *store data*
02750  GOSUB 3030
02760  RETURN
02770  REM *spray acquire data routine*
02790  I=I+1
02800  SETTIME=TIME
02810  SD(1)=COUNTER
02820  GOSUB 3120
02850  REM *USE PIAASTAT AS THE ON-OFF INDICATER,$FFFF=ON,$0=OFF*
02860  SD(4)=INDICATER
02865  FOR M=1 TO 2
02870  AD12N=AD12_4
02880  GOSUB 2090
02890  SD(5)=AD12_4
02895  NEXT M
02900  RETURN
02910  REM *store furnace data routine*
02930  I=I+1
02940  SD(1)=COUNTER
02950  CHAN=0
02960  GOSUB 2030
02970  SD(2)=AD16
02980  GOSUB 3120
03010  SD(4)=PIAASTAT
03020  RETURN
03030  REM *store data routine*
03050  I=I+1
03060  SD(1)=COUNTER
03070  GOSUB 3120
03100  SD(4)=PIAASTAT
03110  RETURN
03120  REM *AD12_0*
03130  FOR M=1 TO 2
03140  AD12N=AD12_0
03150  GOSUB 2090
03160  SD(3)=AD12_0
03170  NEXT M
03180  RETURN
```



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TABLE A1

Modification of Process Parameters

Solution: N-Butyl Zirconate

Sequence: 5-seconds spray, 5-minute heat treatment

| Sample ID | Temp (Furnace) | Number of Coats | Results |
|---|---|---|---|
| Oct.7, 1983 | | | |
| 401 | 500 | 1 | Thin coating, glass cracked |
| 402 | 500 | 1 | " |
| 404 | 500 | 1 | " |
| 405 | 500 | 1 | " |
| 403 | 500 | 1 | " |
| Oct.11, 1983 | | | |
| 407 | 500 | 1 | Glass cracked |
| 408 | 500 | 1 | Thin coating |
| 409 | 500 | 1 | Good coating |
| 410 | 500 | 1 | " |
| 411 | 500 | 5 | " |
| 412 | 500 | 5 | " |
| 413 | 500 | 5 | " |
| 415 | 550 | 1 | Good thin coating |
| 416 | 550 | 1 | " |
| 417 | 550 | 1 | " |
| 418 | 550 | 1 | " |
| 420 | 550 | 5 | Thin coating |
| 427 | 550 | 5 | " |
| 428 | 550 | 5 | " |
| 429 | 550 | 5 | " |
| 430 | 550 | 5 | " |
| 423 | 550 | 5 | " |
| 439 | 550 | 20 | Good coating, slight translucence |



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Table A1 (contd)

| Sample ID | Temp (Furnace) | Number of Coats | Results |
|---|---|---|---|
| 441 | 400 | 1 | Thin and opaque |
| 448 | 400 | 1 | " |
| 450 | 400 | 5 | Thick white opaque film, poor adhesion |
| 451 | 400 | 10 | " " |
| 452 | 700 | 7 | Glass broke due to thermal |
| 454 | 700 | 1 | shock. |
| 456 | 700 | 1 | " " |
| 457 | 700 | 1 | " " |
| 466 | 600 | 1 | Very thin coating |
| 468 | 600 | 1 | " |
| 469 | 600 | 5 | Glass broke |
| 470 | 600 | 5 | Good coating |
| 472 | 600 | 5 | Good coating, clear |
| 474 | 600 | 10 | Good transparent film, slightly opaque. |
| 475 | 600 | 1 | Good coating |
| 476 | 650 | 1 | Glass broke |
| 479 | 650 | 1 | " |
| 481 | 650 | 1 | Thin coating, glass cracked |
| 485 | 650 | 5 | Good film but glass warped. |



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## APPENDIX B

TGA of Butyl Zirconate



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RESEARCH

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January 27, 1984

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**REPORT NUMBER** PS 235-84-2

**IDENTIFICATION** Work Order No. 15076

**SPECIFICATIONS OF ORDER** TGA ON BUTYL ZIRCONATE

## INTRODUCTION

A sample of Butyl Zirconate was submitted for TGA.

## EXPERIMENTAL

The sample was dried in a vacuum oven at 50°C for approximately half hour. TGA was carried out on a DuPont 951 Thermogravimetric Analyzer under the following conditions:

| | |
|---|---|
| atmosphere: | $N_2$ gas |
| flow rate: | 150 cc/min |
| program rate: | 20°C/min |
| suppression: | 0 mg |
| range y: | 10 mv/cm |
| dy: | 5 mv/cm |
| weight: | 14.95 mg |

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RESULTS

The experimental trace shows a weight loss of 10.8% between room temperature and 250°C. This probably represents loss of residual 1-butanol (b.p.117°C). Another weight loss begins at 250°C. By 450°C, a further 69.6% of the original sample weight is lost. Between 450°C and 800°C, no further weight loss occurs.

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Organic Materials Centre



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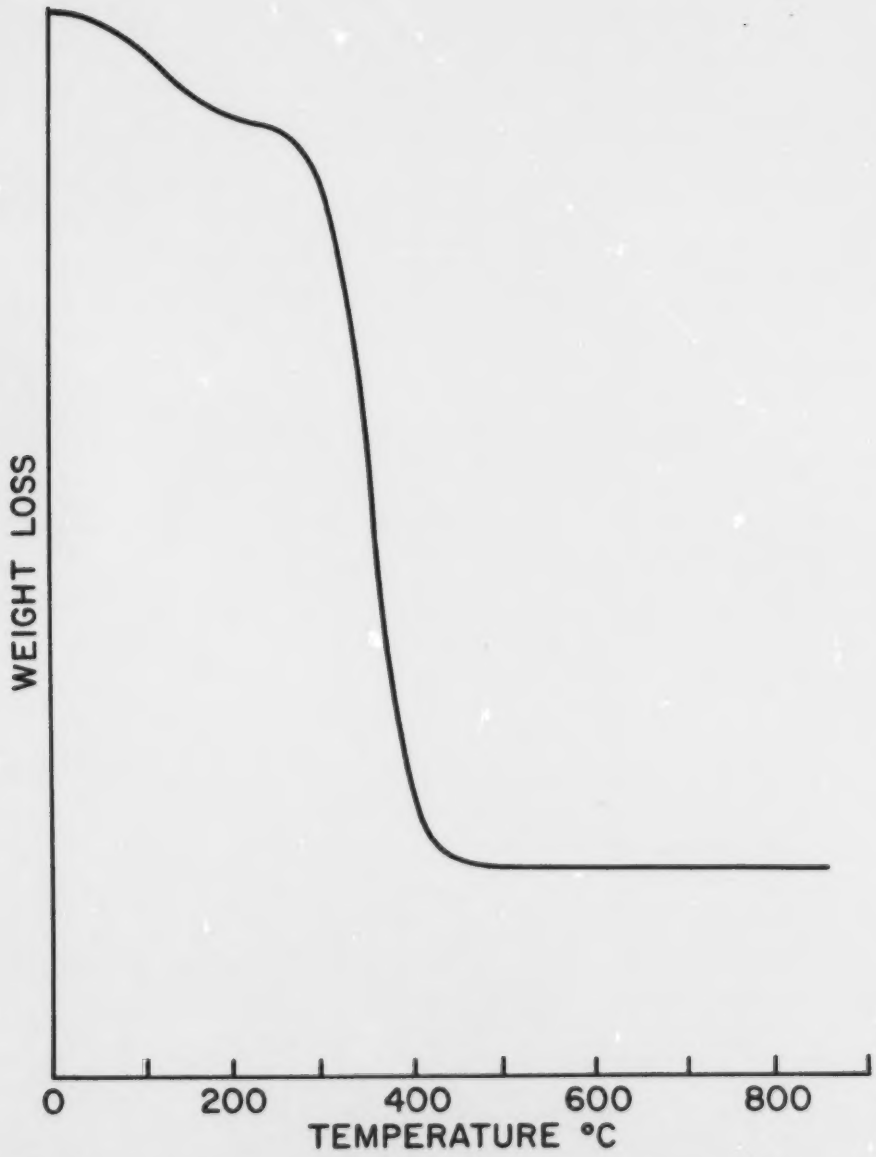


Fig. 2 THERMOGRAVIMETRIC ANALYSIS OF BUTYL ZIRCONATE.



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## APPENDIX C

Evaluations of Different Substrates



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TABLE C1 - Aluminum Substrates

| Aluminum Samples | Coating Condition/each Coat | | | No.of Coats | Final anneal period (min) | Results |
|---|---|---|---|---|---|---|
| | Furnace Temp(°C) | Spraying time (s) | Heat treatment period (min) | | | |
| A 194 | 500 | 2 | 2 | 1 | 2 | Plate bent, brown spots. |
| A 195 | 500 | 2 | 2 | 5 | 2 | Brown spots. |
| A 204 | 550 | 2 | 2 | 5 | 2 | Black coating, cracked. |
| A 205 | 450 | 2 | 2 | 5 | 2 | Brown coating - some cracks |
| A 206 | 400 | 2 | 2 | 5 | 2 | Pale brown coating - some cracks. |
| A 207 | 400 | 2 | 2 | 1 | 2 | Same as above. |
| A 208 | 400 | 2 | 2 | 5 | 2 | Brown and spotty coating |
| A 209 | 400 | 2 | 2 | 1 | 2 | Same as above. |
| A 210 | 450 | 2 | 2 | 5 | 2 | Same as above. |
| A 211 | 450 | 2 | 2 | 1 | 2 | Same as above. |
| A 212 | 450 | 2 | 2 | 1 | 2 | Same as above. |
| A 219 | 500 | 2 | 2 | 1 | 2 | Sample bent, coating is cracked. |
| A 220 | 500 | 2 | 2 | 5 | 2 | Coating is cracked and brown. |
| A 221 | 550 | 2 | 2 | 2 | 2 | Same as above. |
| A 222 | 550 | 2 | 2 | 5 | 2 | Good transparent coating. |
| A 223 | 550 | 2 | 2 | 5 | 2 | Same as above. |
| A 224 | 550 | 2 | 2 | 3 | 2 | Same as above. |
| A 225 | 550 | 2 | 2 | 3 | 2 | Same as above. |
| A 227 | 550 | 2 | 2 | 2 | 2 | Brown coating & cracked |
| A 226 | 550 | 2 | 2 | 1 | 2 | Coating hardly visible. |
| A 228 | 550 | 2 | 2 | 3 | 2 | Good transparent coating. |
| A 229 | 550 | 2 | 2 | 5 | 2 | Same as above. |
| A 230 | 550 | 2 | 2 | 10 | 2 | Excellent coating, transparent. |
| A 231 | 550 | 2 | 2 | 20 | 2 | Same as above. |

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**TABLE C2** **Results of Spray Trials Using N-butyl zirconate on Enamelled Steel**

| Furnace Temperature | Furnace Time | Spray Time | No. of Cycles | Observations |
|---|---|---|---|---|
| 700°C | 6 min | 10 S | 5/NoHT* | Adherent, X-ray: cubic/tetragonal $ZrO_2$ $TiO_2$(anatase) |
| 700°C | 6 min | 10 S | 5/HT* | |
| 500°C | 8 min | 10 S | 3/HT | surface yellow powder |
| 600°C | 7 min | 10 S | 3/HT* | transparent, Newton's ring, X-ray: $ZrO_2$ /$TiO_2$ |
| 700°C | 6 min | 10 S | 3/HT* | " |

* Substrates were heat treated in the furnace subsequent to spraying.



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TABLE C3
Stainless Steel Substrate - 310ss

| Sample ID | Furnace Temp ($^{o}$C) | No. of Coats (5 sec.spray) (5 min. heat) Treatment | Results |
|---|---|---|---|
| 310SS-7 | 500 | 5 | Coating is brown and spotted |
| 310SS-8 | 500 | 1 | Good coating white/grey colour |
| 310SS-9 | 500 | 1 | Same as 8 - appears to have some droplets |
| 310SS-10 | 550 | 1 | Thin grey in centre |
| 310SS-11 | 550 | 5 | Yellowish in centre |
| 310SS-12 | 400 | 1 | Coating is thick and brown - with large black droplets |
| 310SS-13 | 400 | 5 | Powdery, white |
| 310SS-14 | 600 | 5 | Pale blue, good adherence |
| 310SS-15 | 600 | 5 | Same as above - very thin coating |
| 310SS-16 | 600 | 1 | Coating hardly visible |
| 310SS-17 | 600 | 1 | Same as above |
| 310SS-18 | 700 | 1 | Steel is heavily oxidized - it turned blue and purple - coating barely visible |
| 310SS-19 | 700 | 5 | Thin coating - dark yellow to brown |
| 310SS-20 | 700 | 5 | Same as above. |

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Table C3 (contd)

| Sample No | Coating Condition/each Coat | | | No. of Coats | Final anneal period (min) | Results |
|---|---|---|---|---|---|---|
| | Furnace Temp( C) | Spraying time(s) | Heat treatment period (min) | | | |
| 310-22 | 550 | 5 | 5 | 5 | 2 | Coating is brown, good |
| 310-23 | 550 | 5 | 5 | 10 | 2 | Same as above, heavy oxidation on the uncoated good areas. |
| 310-24 | 550 | 5 | 5 | 20 | 2 | Thick and black in the centre, good adherent coating. |
| 310-25 | 550 | 5 | 5 | 5 | 2 | Yellow film, dark brown at centre, heavy oxidation on uncoated areas. |
| 310-26 | 550 | 5 | 5 | 3 | 2 | Thin yellow film. |
| 310-27 | 550 | 5 | 5 | 1 | 2 | Pale grey and yellow film, good. |
| 310-28 | 550 | 5 | 5 | 5 | 2 | Brown coating at centre, good adherence. |
| 310-29 | 550 | 5 | 5 | 3 | 2 | Yellow film. |
| 310-30 | 550 | 5 | 5 | 1 | 2 | Pale yellow film. |
| 310-31 | 500 | 3 | 5 | 1 | 2 | Powdery yellowish brown coating. |
| 310-32 | 500 | 3 | 5 | 3 | 2 | Good coating, grey and yellowish. |
| 310-33 | 500 | 3 | 5 | 1 | 2 | Grey to white with brown spots, good coating |
| 310-34 | 500 | 3 | 5 | 5 | 2 | Uncoated area oxidized coating is dark at centre, good adherence. |
| 310-35 | 500 | 3 | 5 | 10 | 2 | Dark black circle, very thick droplets. |
| 310-36 | 550 | 2 | 2 | 10 | 2 | Thick coating, brown and black. |

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Table C3 (contd)

| Sample No | Coating Condition/each Coat | | | No. of Coats | Final anneal period (min) | Results |
|---|---|---|---|---|---|---|
| | Furnace Temp( C) | Spraying time(s) | Heat treatment period (min) | | | |
| 310-37 | 550 | 2 | 2 | 10 | 2 | Thick dark droplets, problem with the spray system. |
| 310-38 | 550 | 2 | 2 | 5 | 2 | Same as above. |
| 310-39 | 550 | 2 | 2 | 5 | 2 | Same as above. |
| 310-40 | 550 | 2 | 2 | 3 | 2 | Same as above. |
| 310-41 | 550 | 2 | 2 | 1 | 2 | Same as above. |
| 310-42 | 500 | 2 | 2 | 1 | 2 | Same as above. |
| 310-43 | 500 | 2 | 2 | 5 | 2 | Same as above. |
| 310-44 | 500 | 2 | 2 | 3 | 2 | Same as above. |
| 310-45 | 500 | 2 | 2 | 10 | 2 | Same as above. |
| 310-46 | 550 | 2 | 3 | 5 | 2 | Good coating, brown film |
| 310-47 | 550 | 2 | 3 | 3 | 2 | Grey and yellowish film good coating. |
| 310-48 | 550 | 2 | 3 | 1 | 2 | Grey film, good coating |

TABLE C4

304 Stainless Steel Substrate

| Sample No. | Date | Spray Time (sec) | Heat Treatment (min) | No.of Coats | Final anneal (min) | Furnace Temp ($^{o}C$) | Results |
|---|---|---|---|---|---|---|---|
| 1 | Oct.27/83 | 2 | 2 | 1 | 2 | 650 | steel oxidized yellow film |
| 2 | " | 2 | 2 | 1 | 2 | 500 | thin coat |
| 3 | " | 2 | 2 | 5 | 2 | 500 | good coating coloured ring |
| 4 | Nov.25/83 | 2 | 2 | 3 | 2 | 500 | good coat, grey |
| 5 | " | 2 | 2 | 5 | 2 | 500 | good coating |
| 6 | " | 2 | 2 | 1 | 2 | 500 | good coating |
| 7 | Dec.16/83 | 2 | 2 | 3 | 2 | 500 | coating hardly visible |
| 8 | " | 2 | 2 | 3 | 2 | 500 | clear white film |
| 9 | " | 2 | 2 | 1 | 2 | 500 | clear white film |
| 10 | Dec.19/83 | 2 | 2 | 6 | 2 | 500 | thick clear coating |
| 11 | " | 2 | 2 | 6 | 2 | 500 | good $ZrO_2$ film |
| 12 | " | 2 | 2 | 6 | 2 | 500 | good " |
| 13 | " | 2 | 2 | 10 | 2 | 500 | good " |
| 14 | " | 2 | 2 | 10 | 2 | 500 | good " |
| 15 | " | 2 | 2 | 10 | 2 | 500 | good " |
| 16 | Dec.21.83 | 2 | 2 | 20 | 2 | 500 | good " |
| 17 | " | 2 | 2 | 20 | 2 | 500 | good " |
| 18 | " | 2 | 2 | 20 | 2 | 500 | good " |
| 19 | " | 2 | 2 | 3 | 2 | 550 | coating is not visible |

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TABLE C5

Carbon Steel Substrate

| Sample No. | Date | Spray Time (sec) | Heat Treatment (min) | No.of Coats | Final anneal (min) | Furnace Temp ($^{o}$C) | Results |
|---|---|---|---|---|---|---|---|
| 1 | Dec.14/83 | 2 | 2 | 3 | 2 | 500 | good coating |
| 2 | " | 2 | 2 | 3 | 2 | 500 | coating hardly visible |
| 3 | " | 2 | 2 | 3 | 2 | 500 | same as above |
| 4 | Dec.15/83 | 2 | 2 | 6 | 2 | 500 | Brown film |
| 5 | Dec.14/83 | 2 | 2 | 6 | 2 | 500 | Light brown film |
| 6 | Dec.15/83 | 2 | 2 | 3 | 2 | 550 | Light brown film |
| 7 | " | 2 | 2 | 3 | 2 | 550 | Light brown film |
| 8 | " | 2 | 2 | 6 | 2 | 550 | Coating hardly visible |
| 9 | " | 2 | 2 | 6 | 2 | 550 | Problem with the spray system |
| 10 | Dec.23/83 | 2 | 2 | 3 | 2 | 550 | Good white film |
| 11 | " | 2 | 2 | 6 | 2 | 550 | Dark black |
| 12 | " | 2 | 2 | 6 | 2 | 550 | Brown film |
| 13 | " | 2 | 2 | 6 | 2 | 600 | Brown film |
| 14 | " | 2 | 2 | 3 | 2 | 600 | Yellowish film |
| 15 | " | 2 | 2 | 6 | 2 | 500 | Dark brown |
| 16 | " | 2 | 2 | 3 | 2 | 500 | Light brown |
| 17 | Jan.2/84 | 2 | 2 | 6 | 2 | 550 | Good white film good adherence |
| 18 | " | 2 | 2 | 6 | 2 | 600 | Brown film |
| 19 | " | 2 | 2 | 3 | 2 | 600 | Light brown |
| 20 | " | 2 | 2 | 3 | 2 | 500 | Light brown |
| 21 | " | 2 | 2 | 6 | 2 | 500 | Brown and blue film poor coating |



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TABLE C6

Nickel plated Mild Steel Substrate

| Sample No. | Date | Spray Time (sec) | Heat Treatment (min) | No.of Coats | Final anneal (min) | Furnace Temp ($^{o}$C) | Results |
|---|---|---|---|---|---|---|---|
| 1 | Dec.14/83 | 2 | 2 | 3 | 2 | 500 | Blue yellow film - Newton-ring |
| 2 | " | 2 | 2 | 3 | 2 | 500 | " " |
| 3 | " | 2 | 2 | 3 | 2 | 500 | Blue film |
| 4 | " | 2 | 2 | 3 | 2 | 500 | Blue film |
| 5 | " | 2 | 2 | 3 | 2 | 500 | Blue film |
| 6 | " | 2 | 2 | 3 | 2 | 550 | Coloured Newton-ring |
| 7 | " | 2 | 2 | 3 | 2 | 550 | Good coating |
| 8 | " | 2 | 2 | 3 | 2 | 550 | Good coating |
| 9 | " | 2 | 2 | 3 | 2 | 550 | Good coating |

TABLE C7

TiC Coated Carbon Steel

| Sample No. | Date | Spray Time (sec) | Heat Treatment (min) | No.of Coats | Final anneal (min) | Furnace Temp ($^{o}$C) | Results |
|---|---|---|---|---|---|---|---|
| 1 | Dec.13/83 | 2 | 2 | 1 | 2 | 500 | Brown coating |
| 2 | " | 2 | 2 | 1 | 2 | 500 | Yellowish film |
| 3 | " | 2 | 2 | 3 | 2 | 500 | Yellowish film |
| 4 | " | 2 | 2 | 3 | 2 | 500 | Thin clear coating |
| 5 | " | 2 | 2 | 6 | 2 | 500 | Good coating |
| 6 | " | 2 | 2 | 6 | 2 | 500 | Droplets, problem with |
| 7 | Dec.14/83 | 2 | 2 | 3 | 2 | 550 | the spray system |
| 8 | " | 2 | 2 | 3 | 2 | 550 | " " |
| 9 | " | 2 | 2 | 6 | 2 | 550 | Clear, good coating |



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Fig. C1 Nickel plated mild steel coated $ZrO_2$ Film

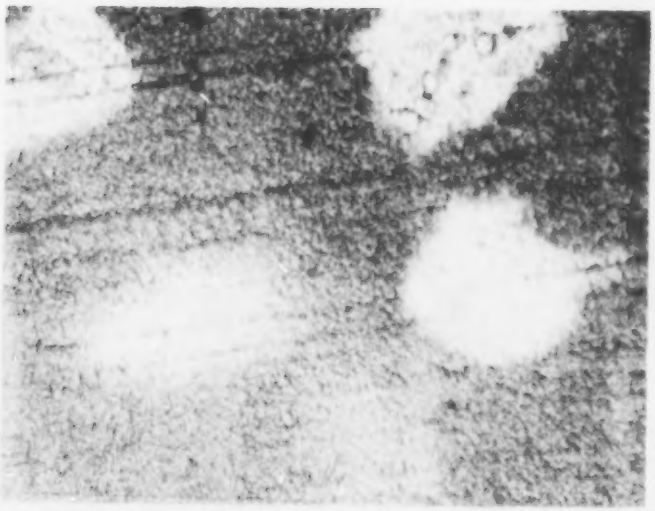

Fig. C2 Nickel plated mild steel uncoated

## APPENDIX D

Abrasion Resistance of $ZrO_2$ Films on Glass



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The abrasion resistance of thin films is difficult to measure due to the thinness of the film and the non-existence of applicable standards for abrasion measurements for thin ceramic coatings.

Therefore, a systematic program was conducted to evaluate the parameters which affected the wear index results. Two of the most important steps involved in the abrasion measurement were found to be the measurement of sample weight before and after the abrasion test and the selection of wheel type and cycling schedules.

Procedures for Weight Measurement

The abrasion test was carried out in several sequences (see Fig. D1). It was observed that the time lapsed between steps 1 and 2 and between steps 4 and 5 strongly affected the measured weight loss of glass samples. The importance of the time factor is demonstrated in Table D1. It can be seen that the weight of sample increases as a function of time and only stabilizes after 30 minutes in air.

The time between steps 1 and 2 and between steps 4 and 5 must, therefore, be maintained to about 1/2 hour.

Abrader Wheel and Cycling Schedules

Using the preparatory cleaning and weighing procedures outlined in section 2.1, three different wheel types were evaluated in the development of the more suitable operating parameters. Uncoated glass samples and wheel type : Calibrate H10, H18, H38 (Taber Instrument Corp.) were utilized with different cycling schedules.

The experimental data (Table D2) are plotted in Fig. D2. This chart indicated that in order to achieve consistency in the abrasion results, a weight loss of about 15-20 mg is required. The following operating conditions were therefore selected:

- Wheel type H10
- Cycling schedule: 35
- Load: 1,000g
- Glass sample: 4"x4"

The most suitable ASTM standard was ASTM D4060-81. Testing procedures based on this standard were used.



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Figure D1

Abrasion Test of Thin Oxide Film-Measurement Procedure

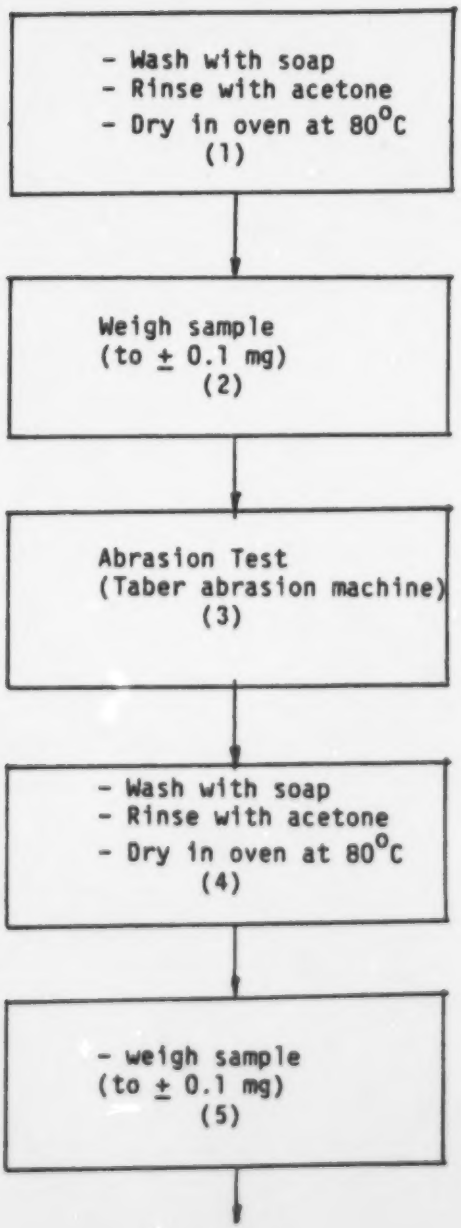




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TABLE D1

Weight Variation vs Time

| Time (Min) Time duration after removing sample from the oven | Wt (g) Glass 1 | Glass 2 | Glass 3 | Glass 4 | Glass 5 |
|---|---|---|---|---|---|
| | #499 | #500 | #501 | #477 | #478 |
| 5 | 126.8600 | 128.4388 | 126.2390 | 127.2565 | 128.3775 |
| 10 | 126.8620 | 128.4411 | 126.2418 | 127.2576 | 128.3789 |
| 15 | 126.8631 | 128.4420 | 126.2422 | 127.2580 | 128.3790 |
| 20 | 126.8634 | 128.4425 | 126.2430 | 127.2586 | 128.3789 |
| 25 | 126.8634 | 128.4425 | 126.2438 | 127.2589 | 128.3795 |
| 30 | 126.8638 | 128.4429 | 126.2429 | 127.2589 | 128.3799 |
| 35 | 126.8640 | 128.4430 | 126.2430 | 127.2590 | 128.3800 |
| 40 | 126.8640 | 128.4431 | 126.2430 | 127.2590 | 128.3800 |
| 45 | 126.8640 | 128.4432 | 126.2431 | 127.2592 | 128.3800 |
| 50 | 126.8640 | 128.4432 | 126.2431 | 127.2591 | 128.3801 |
| 55 | 126.8641 | 128.4432 | 126.2432 | 127.2592 | 128.3801 |
| 60 | 126.8641 | 128.4432 | 126.2432 | 127.2592 | 128.3801 |

## TABLE D2

### Abrasion Resistance Evaluation of Uncoated Glass

| Sample No. | No. DF Cycle | Wheel Type | Load (g) | Weight of Sample before | Weight after (g) | Wt loss (mg) | Wear Index |
|---|---|---|---|---|---|---|---|
| 500 | 20 | H18 | 500 | 128.4429 | 128.4364 | 6.5 | 325 |
| 501 | 20 | H18 | 500 | 126.2429 | 126.2327 | 10.2 | 510 |
| 505 | 20 | H18 | 500 | 127.5179 | 127.5149 | 3.0 | 150 |
| 526 | 10 | H18 | 500 | 119.7557 | 119.7549 | .8 | 80 |
| 527 | 10 | H18 | 500 | 120.8341 | 120.8330 | 1.1 | 110 |
| 502 | 40 | H18 | 500 | 128.7435 | 128.7348 | 8.7 | 217.5 |
| 503 | 40 | H18 | 500 | 126.9827 | 126.9745 | 8.2 | 205 |
| 504 | 40 | H18 | 500 | 130.2130 | 130.2071 | 5.9 | 147.5 |
| 506 | 20 | H38 | 500 | 127.7640 | 127.7639 | .1 | 10 |
| 507 | 20 | H38 | 500 | 127.7469 | 127.7460 | .9 | 45 |
| 508 | 20 | H38 | 500 | 128.4419 | 128.4422 | -.3 | - |
| 509 | 40 | H38 | 500 | 126.5213 | 126.5215 | -.2 | - |
| 510 | 40 | H38 | 500 | 130.1409 | 130.1414 | -.5 | - |
| 524 | 40 | H38 | 500 | 120.5751 | 120.5729 | 2.2 | 55 |
| 525 | 41 | H38 | 500 | 120.0984 | 120.0919 | 2.9 | 70.7 |
| 528 | 30 | H38 | 500 | 122.5864 | 122.5860 | .4 | 13.3 |
| 529 | 30 | H38 | 500 | 119.2140 | 119.2155 | -1.5 | - |
| 504A | 40 | H18 | 500 | 130.2071 | 130.1987 | 8.4 | 210 |
| 507A | 40 | H18 | 500 | 127.7460 | 127.7394 | 6.6 | 165 |
| 500A | 40 | H18 | 500 | 128.4364 | 128.4282 | 8.2 | 205 |
| 524A | 40 | H18 | 500 | 120.5729 | 120.5663 | 6.6 | 150 |
| 525A | 20 | H18 | 500 | 120.0919 | 120.0898 | 2.1 | 105 |
| 526A | 20 | H18 | 500 | 119.7557 | 119.7526 | 3.1 | 155 |
| 505A | 40 | H38 | 1000 | 127.5149 | 127.5156 | .7 | 17.5 |
| 502A | 40 | H38 | 1000 | 128.7348 | 128.7340 | .8 | 20 |
| 503A | 40 | H18 | 1000 | 126.9745 | 126.9618 | 12.7 | 317.5 |



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Table D2 (contd.)

| Sample No. | No. DF Cycle | Wheel Type | Load (g) | Weight of Sample before | Weight after (g) | Wt loss (mg) | Wear Index |
|---|---|---|---|---|---|---|---|
| 508A | 40 | H18 | 1000 | 128.4422 | 128.4351 | 7.1 | 177.5 |
| 506A | 40 | H10 | 1000 | 127.7639 | 127.7471 | 16.8 | 420 |
| 509A | 40 | H10 | 1000 | 126.5215 | 126.5040 | 17.5 | 437.5 |
| 510A | 20 | H10 | 1000 | 130.1414 | 130.1316 | 9.8 | 490 |
| 501A | 20 | H10 | 1000 | 126.2327 | 126.2339 | -1.2 | - |
| 533 | 35 | H10 | 1000 | 127.3552 | 127.3414 | 13.8 | 394 |
| 532 | 35 | H10 | 1000 | 123.6822 | 123.6688 | 14.5 | 414 |
| 534 | 35 | H10 | 1000 | 126.9185 | 126.9050 | 13.5 | 386 |
| 535 | 35 | H10 | 1000 | 130.1461 | 130.1313 | 14.8 | 423 |
| 536 | 35 | H10 | 1000 | 127.9340 | 127.9196 | 14.4 | 411 |
| 537 | 35 | H10 | 1000 | 126.9155 | 126.9010 | 14.5 | 414 |
| 538 | 35 | H10 | 1000 | 128.7810 | 128.7678 | 13.2 | 377 |
| 539 | 35 | H10 | 1000 | 129.1004 | 129.0819 | 18.5 | 528 |
| 540 | 35 | H10 | 1000 | 123.7384 | 123.7252 | 13.2 | 377 |

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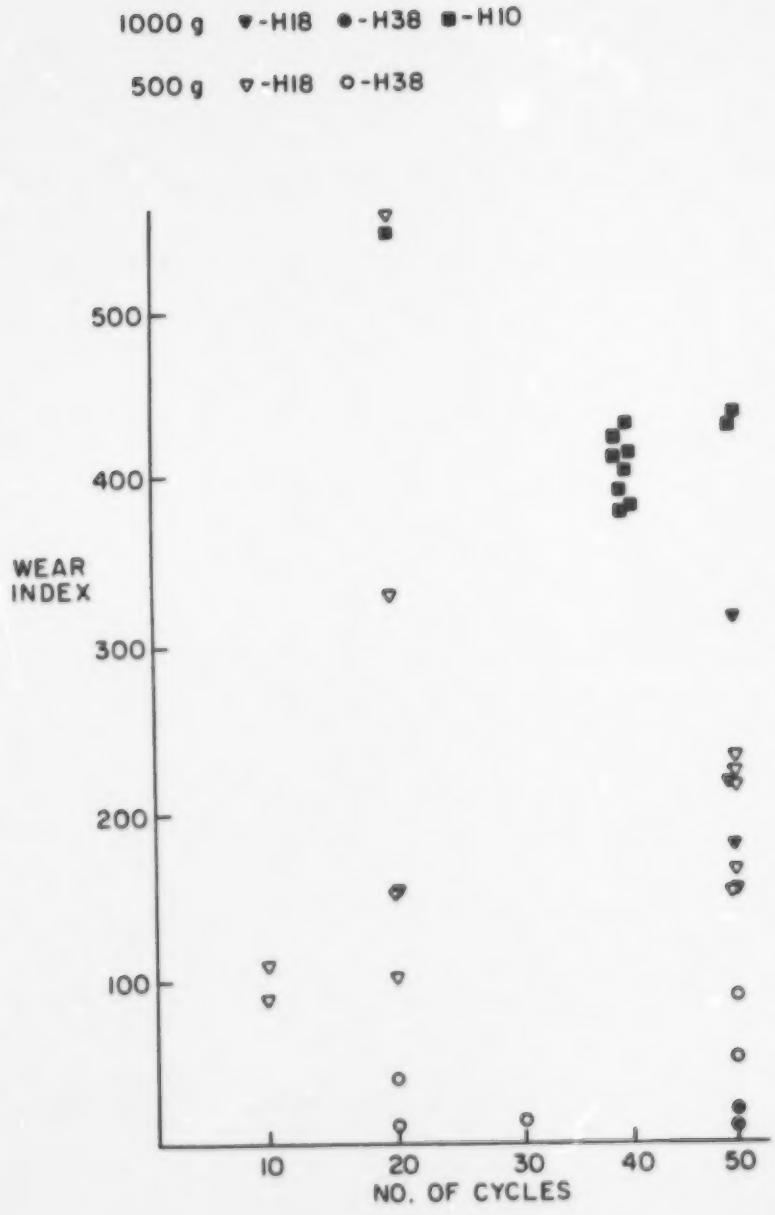
Figure D2 EVALUATION OF ABRASION PARAMETERS



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Designation: D 4060 – 81

# Standard Test Method for ABRASION RESISTANCE OF ORGANIC COATINGS BY THE TABER ABRASER[1]

This standard is issued under the fixed designation D 4060; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

## 1. Scope

1.1 This method covers the determination of the resistance of organic coatings to abrasion produced by the Taber Abraser on coatings applied to a plane, rigid surface, such as a metal panel.

1.2 Because of the poor reproducibility of this method, it should be restricted to testing in only one laboratory when numerical abrasion resistance values are to be used. Interlaboratory agreement is improved significantly when rankings of coatings are used in place of numerical values.

## 2. Applicable Documents

2.1 *ASTM Standards*:

D 823 Producing Films of Uniform Thickness of Paint, Varnish, Lacquer, and Related Products on Test Panels[2]

D 1005 Measurement of Dry Film Thickness of Organic Coatings[2]

D 1186 Nondestructive Measurement of Dry Film Thickness of Nonmagnetic Coatings Applied to a Ferrous Base[2]

D 1400 Nondestructive Measurement of Dry Film Thickness of Nonconductive Coatings Applied to a Nonferrous Metal Base[2]

D 2240 Test for Rubber Property—Durometer Hardness[3]

## 3. Summary of Method

3.1 In this method, the organic coating is applied at uniform thickness to a plane, rigid panel and, after curing, the surface is abraded by rotating the panel under weighted abrasive wheels.

3.2 Abrasion resistance is expressed as loss in weight at a specified number of abrasion cycles, as loss in weight per cycle, and as number of cycles required to remove a unit amount of coating thickness.

## 4. Description of Terms

4.1 *wear index*—1000 times the loss in weight in milligrams per cycle.

4.2 *weight loss*—the loss in weight in milligrams, determined at a specified number of cycles.

4.3 *wear cycles per mil*—the number of cycles of abrasion required to wear a film through to the substrate per mil of film thickness.

## 5. Apparatus

5.1 *Taber Abraser.*[4]

5.2 *Abrasive Wheels*—Resiliant calibrase wheels No. CS-10 or CS-17, as required, shall be used. Because of the slow hardening of the rubber bonding material in this type of wheel, the wheels should not be used after the date marked on them, or one year after their purchase, if the wheels are not dated.

NOTE 1—The hardness of the wheel can be checked by Method D 2240. An acceptable durometer hardness value is 72 ±5.

5.3 *Resurfacing Medium*, an S-11 abrasive

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[1] This method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings and Materials and is the direct responsibility of Subcommittee D01.23 on Physical Properties of Applied Paint Films.

Current edition approved Oct. 30, 1981. Published December 1981.

[2] *Annual Book of ASTM Standards*, Part 27.

[3] *Annual Book of ASTM Standards*, Parts 35 and 37.

[4] Available from Teledyne Taber, North Tonawanda, N. Y. 14120.



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disc, used for resurfacing the abrasion wheels.

5.4 *Vacuum Pick-Up Assembly*, consisting of a vacuum unit, a variable transformer suction regulator, a nozzle with bracket attachment, and a connecting hose with adaptor.

## 6. Test Specimens

6.1 Apply uniform coating of the material to be tested to a plane, rigid panel. Specimens shall be a disc 4 in. (100 mm) in diameter or a plate 4 in. (100 mm) square with rounded corners and with a ¼-in. (6.3-mm) hole centrally located on each panel. Prepare a minimum of two coated panels for the material.

NOTE 2—The coatings should be applied in accordance with Method D 823, or as agreed upon by the purchaser and the seller.

NOTE 3—The thickness of the dry coatings should be measured in accordance with Methods D 1005, D 1186, or D 1400.

## 7. Standardization

7.1 Mount the selected abrasive wheels on their respective flange holders, taking care not to handle them by their abrasive surfaces. Adjust the load on the wheels to 1000 g.

7.2 Mount the resurfacing medium on the turntable. Lower the abrading heads carefully until the wheels rest squarely on the test film. Place the vacuum pickup nozzle in position and adjust it to a distance of 1/32 in. (1 mm) above the test film.

7.3 Set the counter to "zero" and set the suction regulator to approximately 50 points on the dial. The setting may be increased to 90 if more effective removal of the abradings appears necessary.

7.4 Start the vacuum pickup and then the turntable of the abrader. Resurface the wheels by running them 50 cycles against the resurfacing medium.

NOTE 4—The wheels should be resurfaced in this manner before testing each specimen and after every 500 cycles.

## 8. Conditioning

8.1 Cure the coated panel under conditions of humidity and temperature as agreed upon between purchaser and seller.

8.2 Unless otherwise agreed upon between purchaser and seller, condition the coated panel for at least 24 h at 23 ±2°C and 50 ±5 % relative humidity. Conduct the test in the same environment or immediately on removal therefrom.

## 9. Procedure

9.1 Weigh the test specimen to the nearest 0.1 mg and record this weight, if either the wear index or the weight loss is to be reported.

9.2 Measure the coating thickness of the test specimen in several locations along the path to be abraded.

9.3 Mount the test specimen on the turntable. Place the abrading heads on the test film and the vacuum pickup nozzle in position as outlined in 7.4. Set the counter and suction regulator as outlined in 7.5.

9.4 Start the vacuum pickup and then the turntable of the abrader. Subject the test specimen to abrasion for the specified number of cycles or until wear through of the coating is observed. In determining the point of wear through, stop the instrument at intervals for examination of the test specimen.

NOTE 5—It may be advantageous to even out the coating surface by running 200 cycles before the start of the official test.

9.5 Remove any loose abradings remaining on the test specimen by light brushing. Reweigh the test specimen.

9.6 Repeat 9.1 to 9.5 on at least one additional test specimen of the material under test.

## 10. Calculations

10.1 *Wear Index*—Compute the wear index of a test specimen as follows:

$$\text{wear index} = \frac{(A - B)\,1000}{C}$$

where:

$A$ = weight of test specimen before abrasion, mg,
$B$ = weight of test specimen after abrasion, mg, and
$C$ = number of cycles of abrasion recorded.

10.2 *Weight Loss*—Compute weight loss of the test specimen as follows:

$$\text{weight loss} = A - B$$

where:

$A$ = weight of test specimen before abrasion, mg, and
$B$ = weight of test specimen after abrasion, mg.

10.3 *Wear Cycles Per Mil*—Compute the



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wear cycles per mil of the test specimen as follows:

$$\text{wear cycles per mil} = C/T$$

where:

$C$ = number of cycles of abrasion required to wear coating through to substrate and

$T$ = thickness of coating, mils (0.001 in.) (to one decimal place).

NOTE 6— In calculating the wear cycles, it is advisable to discard the first and last readings because the first may be affected by an uneven surface and the last by abrasion of parts of the substrate.

## 11. Report

11.1 The report shall include the following for each test material:

11.1.1 Temperature and humidity during conditioning and at the time of testing,

11.1.2 Thickness of coating when wear cycles are specified,

11.1.3 Kind of calibrase abrasive wheels used,

11.1.4 Load applied to the abrasive wheels,

11.1.5 Number of wear cycles recorded for each test specimen,

11.1.6 Wear index, weight loss, or wear cycles per mil for each test specimen, and

11.1.7 Mean and range of the values of the replicate coated panels.

## 12. Precision

12.1 On the basis of an interlaboratory test of this method in which operators in five laboratories tested four coatings having a broad range of abrasion resistance, the within-laboratories coefficients of variation and between-laboratories coefficients of variation were found to be those in Table 1. Based upon these coefficients, the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

12.1.1 *Repeatability*—Two results by the same operator should be considered suspect if they differ by more than the maximum allowable difference values shown in Table 1.

12.1.2 *Reproducibility*—Two results obtained by operators in different laboratories should be considered suspect if they differ by more than the maximum allowable differences values shown in Table 1.

TABLE 1 Precision of Tabor Abrasion Values

| | Within Laboratories | | Between Laboratories | |
|---|---|---|---|---|
| | Coefficient of Variation, % | Maximum Allowable Difference, % | Coefficient of Variation, % | Maximum Allowable Difference, % |
| Weight loss at 500 cycles | 12 | 48 | 36 | 105 |
| Weight loss at 1000 cycles | 10 | 46 | 30 | 90 |
| Wear index at 500 cycles | 13 | 52 | 36 | 106 |
| Wear index at 1000 cycles | 10 | 46 | 30 | 92 |
| Cycles per mil | 13 | 44 | 31 | 92 |

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*This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, Pa. 19103, which will schedule a further hearing regarding your comments. Failing satisfaction there, you may appeal to the ASTM Board of Directors.*



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## TABLE D3

## Abrasion Resistance Evaluation

Parameters: Taber Abrader
Load: 1000g/Abrader Wheel: Calibrade H10
Number of Cycles: 35/Sample: Glass 4"x4"

| Sample | Wt Before (g) | Wt After (g) | Spray Condition | Wt Loss (mg) | Wear Index | Avg.Wear Index |
|---|---|---|---|---|---|---|
| 585 | 119.3994 | 119.3968 | 550° | 2.6 | 74.3 | 150.65 |
| 596 | 125.2925 | 125.2903 | 1 coat | 2.2 | 62.9 | " |
| 598 | 124.1171 | 124.1108 | " | 6.3 | 180 | " |
| 611 | 124.0386 | 124.0339 | " | 6.3 | 180 | " |
| 612 | 121.5834 | 121.5747 | " | 8.7 | 248.6 | " |
| 616 | 124.4401 | 124.1368 | " | 3.3 | 94.3 | " |
| 617 | 123.9172 | 123.9114 | " | 5.8 | 165.7 | " |
| 618 | 123.0290 | 123.0231 | " | 5.9 | 168.6 | " |
| 620 | 123.3624 | 123.3585 | " | 3.9 | 111.4 | " |
| 622 | 123.2874 | 123.2823 | " | 5.1 | 145.7 | " |
| 624 | 131.4681 | 131.4602 | " | 7.9 | 225.7 | " |
| 568 | 119.9382 | 119.9337 | 550° | 4.5 | 128.6 | 133.25 |
| 577 | 125.4088 | 125.4060 | 5 coats | 2.8 | 80 | " |
| 578 | 122.6653 | 122.6626 | " | 2.7 | 77.1 | " |
| 580 | 121.3127 | 121.3094 | " | 3.3 | 94.3 | " |
| 588 | 123.5680 | 123.5653 | " | 2.7 | 77.1 | " |
| 594 | 122.4987 | 122.4937 | " | 5.0 | 142.9 | " |
| 600 | 122.9028 | 122.8953 | " | 7.5 | 214.3 | " |
| 604 | 121.8334 | 121.8303 | " | 3.1 | 88.6 | " |
| 605 | 123.7376 | 123.7328 | " | 4.8 | 137.1 | " |
| 628 | 126.5382 | 126.5294 | " | 8.8 | 251.4 | " |
| 630 | 124.6126 | 124.6065 | " | 6.1 | 174.3 | " |



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Table D3 (continued)

| Sample | Wt Before (g) | Wt After (g) | Spray Condition | Wt Loss (mg) | Wear Index | Avg.Wear Index |
|---|---|---|---|---|---|---|
| 566 | 127.0683 | 127.0600 | 550° | 8.3 | 237.1 | 197.85 |
| 570 | 122.3265 | 122.3209 | 10 coats | 5.6 | 160 | " |
| 583 | 121.0773 | 121.0728 | " | 4.5 | 128.6 | " |
| 591 | 122.9045 | 122.9004 | " | 4.1 | 117.1 | " |
| 601 | 124.2363 | 124.2281 | " | 8.2 | 234.3 | " |
| 603 | 122.5450 | 122.5392 | " | 5.8 | 165.7 | " |
| 606 | 124.7110 | 124.7057 | " | 5.3 | 151.4 | " |
| 608 | 123.2396 | 123.2312 | " | 8.4 | 240 | " |
| 613 | 125.4704 | 125.4614 | " | 9.0 | 257.1 | " |
| 615 | 124.3572 | 124.3504 | " | 6.8 | 194.3 | " |
| 627 | 110.8748 | 110.8657 | " | 9.1 | 260 | " |
| 629 | 125.7383 | 125.7303 | " | 8.0 | 228.6 | " |
| 567 | 126.5110 | 126.5074 | 550° | 3.6 | 102.9 | 198.11 |
| 571 | 127.6388 | 127.6319 | 20 coats | 6.9 | 197.1 | " |
| 575 | 125.7512 | 125.7456 | " | 5.6 | 160 | " |
| 579 | 119.4649 | 119.4556 | " | 9.3 | 265.7 | " |
| 581 | 127.8737 | 127.8699 | " | 3.8 | 108.6 | " |
| 582 | 120.9283 | 120.9210 | " | 7.3 | 208.6 | " |
| 586 | 123.4660 | 123.4573 | " | 8.7 | 248.6 | " |
| 587 | 122.8137 | 122.8066 | " | 7.1 | 202.9 | " |
| 589 | 123.7627 | 123.7546 | " | 8.1 | 231.4 | " |
| 590 | 123.6629 | 123.6563 | " | 6.6 | 188.6 | " |
| 592 | 120.7368 | 120.7262 | " | 10.6 | 302.9 | " |
| 607 | 121.4515 | 121.4459 | " | 5.6 | 160 | " |
| 633 | 125.2526 | 125.2453 | 650° | 7.3 | 208.6 | 227.98 |
| 637 | 125.6189 | 125.6113 | 1 coat | 7.6 | 217.1 | " |
| 640 | Broke | | " | - | - | " |
| 641 | 125.3834 | 125.3760 | " | 7.4 | 211.4 | " |
| 642 | 125.3654 | 125.3554 | " | 10.0 | 285.7 | " |
| 649 | 124.4817 | 124.4741 | " | 7.6 | 217.1 | " |

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Table D3 (continued)

| Sample | Wt Before (g) | Wt After (g) | Spray Condition | Wt Loss (mg) | Wear Index | Avg.Wear Index |
|---|---|---|---|---|---|---|
| 477 | 127.2579 | 127.2542 | Uncoated | 3.7 | 105.7 | 103.41 |
| 458A | 125.2452 | 125.2440 | " | 1.2 | 34.3 | " |
| 531A | 126.1087 | 126.1040 | " | 4.7 | 134.3 | " |
| 532A | 123.6665 | 123.6605 | " | 6.0 | 171.4 | " |
| 533A | 127.3399 | 127.3353 | " | 4.6 | 131.4 | " |
| 535A | 130.1294 | 130.1265 | " | 2.9 | 82.8 | " |
| 536A | 127.9177 | 127.9143 | " | 3.4 | 97.1 | " |
| 537A | 126.8989 | 126.8949 | " | 4.0 | 114.3 | " |
| 538A | 128.7657 | 128.7632 | " | 2.5 | 71.4 | " |
| 540A | 123.7234 | 123.7202 | " | 3.2 | 91.4 | " |
| 652 | 128.7436 | 128.7396 | Uncoated | 4.0 | 114.3 | 118.47 |
| 653 | 129.2809 | 129.2774 | " | 3.5 | 100 | " |
| 654 | 129.8189 | 129.8103 | " | 8.6 | 245.7 | " |
| 655 | 135.3115 | 135.3078 | " | 3.7 | 105.7 | " |
| 656 | 131.9477 | 131.9449 | " | 2.8 | 80 | " |
| 657 | 131.9478 | 131.9443 | " | 3.5 | 100 | " |
| 658 | 130.4523 | 130.4466 | " | 5.7 | 139.0 | " |
| 659 | 132.2792 | 132.2753 | " | 3.9 | 111.4 | " |
| 660 | 131.8050 | 131.8017 | " | 3.3 | 94.3 | " |
| 661 | 130.8391 | 130.8358 | " | 3.3 | 94.3 | " |



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TABLE D4

Statistical Analysis of Abrasion Results

| Sample ID | No.of Sample (N) | Sample Variance (S) | Population Variance ($\sigma$) | Average Results $\bar{X}$ | Alternative hypothesis $\bar{X}$*uncoated$\langle\bar{X}$*coated Percent of Confidence |
|---|---|---|---|---|---|
| Uncoated | 20 | 42.42 | 41.35 | 110.94 | - |
| Single coat 550°C | 11 | 59.80 | 57.02 | 150.65 | 95 |
| Five coats 550°C | 11 | 59.15 | 56.40 | 133.25 | 70 |
| Ten coats 550°C | 12 | 51.27 | 49.09 | 197.85 | 99 |
| Twenty coats 550°C | 12 | 59.85 | 57.30 | 198.10 | 99 |
| Single coat 650°C | 5 | 32.47 | 29.04 | 227.98 | 99 |



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## APPENDIX E

Thickness Measurement of $ZrO_2$ Films



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**MEMO**

E1
ONTARIO RESEARCH FOUNDATION

SHERIDAN PARK RESEARCH COMMUNITY
MISSISSAUGA, ONTARIO, CANADA L5K 1B3 • (416) 822-4111 • TELEX 06-982311

December 6, 1983

TO: Dat Nguyen, MG&C

FROM: Bob Gallinger, ES/M&I

Subject: Your W.O. 15083 - thickness of $ZrO_2$ films

THICKNESS MEASUREMENT OF ZIRCONIA FILMS

It has not been possible to determine the actual thickness of the film on the samples supplied for thickness measurement using the Sloan M-100 Angstrometer, due to the poor film surface quality and the poor edge definition between the glass substrate and the film material.

The values given below are estimates of the minimum film thickness only. Actual film thicknesses may be greater than these values.

| | | | |
|---|---|---|---|
| #552 | 1 coat | 1000Å | (Fig E1) |
| #555 | 2 coats | 5000Å | (Fig E2) |
| #559 | 3 coats | 4000Å | (Fig E3) |
| #561 | 5 coats | 2000Å | (Fig E4) |
| #563 | 10 coats | 12000Å | (Fig E5) |

Polaroid photos numbered as above show the nonuniformity of the film edge as well as the poor surface quality in the samples. It can be seen from these photos that the surface quality of the films decreases with the number of films of material coated. i.e. surface quality for 1 coat is much better than for 10 or 20 coat samples.

Attached are the "Sample Preparation" sheets taken from the "Sloan M-100 Angstrometer Instruction manual". Please refer to this information when preparing any future samples for Thickness Measurement.

Bob Gallinger



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## SAMPLE PREPARATION

Generally a standard microscope glass slide can be used for monitoring purposes, however, if extreme accuracy is desired the use of an optically flat sample plate such as the Sloan P/N 107-368 Quartz Flat is recommended.

Any one of several methods of masking the monitor slide may be employed to produce the step as shown in Figure E1.

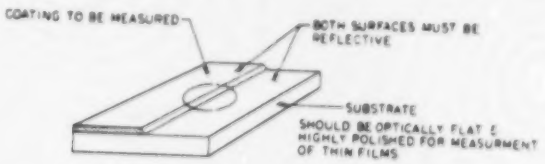
COATING TO BE MEASURED
BOTH SURFACES MUST BE REFLECTIVE
SUBSTRATE
SHOULD BE OPTICALLY FLAT & HIGHLY POLISHED FOR MEASURMENT OF THIN FILMS

Figure E1

However, for thicker film measurement (>2500Å) it is necessary to locate the mask above the monitor slide in such a manner to provide a graded step such as illustrated in Figure E2.

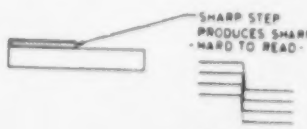


Figure E2A

Figure E2B

As can be seen in Figure E2B it is necessary to count the number of offset fringe lines to calculate total thickness.



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A simple and effective method of masking is shown in Figure E3 employing only a piece of wire. This technique allows greater accuracy of measurement both visually with the micrometer eye-piece and on film, particularly if the specimen is not optically flat thus producing curved fringe lines.

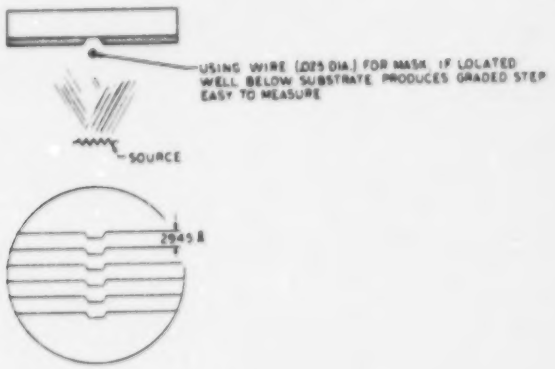


Figure E3



ORF

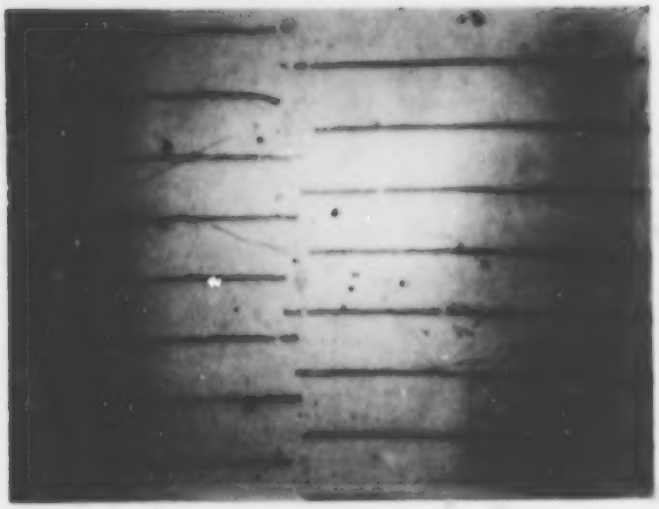

Fig. E4 Sample 552, 1 coat

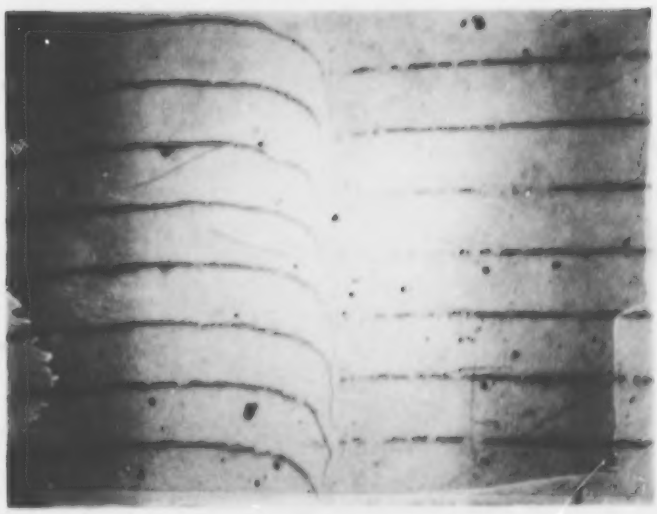

Fig. E5 Sample 555, 2 coats

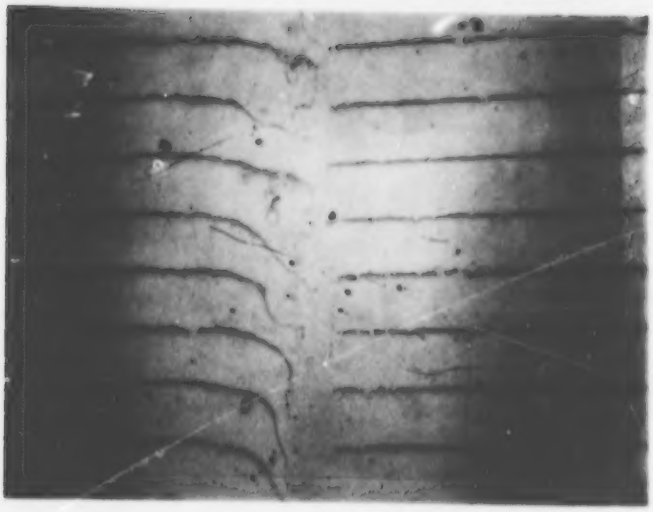

Fig. E6 Sample 559, 3 coats

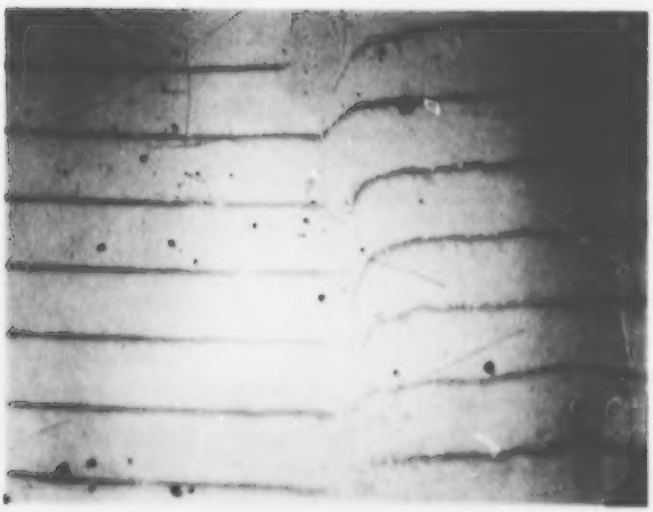

Fig. E7 Sample 561, 5 coats

Fig. E8 Sample 563, 10 coats

## APPENDIX F

Abrasion Resistance of Aluminum



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TABLE F1

Abrasion Test on Aluminum

Weight: 1,000 gm; Abrader Wheels: H-10; No. of Cycles: 35

| Sample # | Spray Conditions | Wt. Loss (mg) | Wear Index | Avg.Wear Index |
|---|---|---|---|---|
| 342 | Uncoated | 13.9 | 397.1 | 323.82 |
| 343 | " | 13.1 | 374.3 | " |
| 344 | " | 10.1 | 288.6 | " |
| 345 | " | 11.2 | 320.0 | " |
| 346 | " | 12.1 | 345.7 | " |
| 347 | " | 10.6 | 302.9 | " |
| 348 | " | 12.3 | 351.4 | " |
| 349 | " | 10.0 | 285.7 | " |
| 350 | " | 10.6 | 302.9 | " |
| 351 | " | 11.2 | 320.0 | " |
| 352 | " | 10.3 | 294.3 | " |
| 353 | " | 10.6 | 302.9 | " |
| 263 | 550° 1 coat | 8.4 | 240.0 | 254.51 |
| 299 | " | 8.6 | 245.7 | " |
| 304 | " | 10.0 | 285.7 | " |
| 305 | " | 7.9 | 225.7 | " |
| 308 | " | 8.3 | 237.1 | " |
| 311 | " | 9.6 | 274.2 | " |
| 312 | " | 9.0 | 257.1 | " |
| 313 | " | 10.3 | 294.3 | " |
| 314 | " | 8.6 | 245.7 | " |
| 315 | " | 9.2 | 262.9 | " |
| 316 | " | 8.4 | 240.0 | " |
| 301 | " | 8.6 | 245.7 | " |



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Table F1 (continued)

| Sample # | Spray Conditions | Wt. Loss (mg) | Wear Index | Avg.Wear Index |
|---|---|---|---|---|
| 265 | 550° 5 coats | 10.1 | 288.6 | 269.08 |
| 271 | " | 9.3 | 265.7 | " |
| 275 | " | 7.1 | 202.9 | " |
| 282 | " | 4.4 | 125.7 | " |
| 288 | " | 7.8 | 222.9 | " |
| 298 | " | 11.9(40 cycles) | 297.5 | " |
| 300 | " | 10.5 | 300.0 | " |
| 303 | " | 10.1 | 288.6 | " |
| 306 | " | 11.0 | 314.3 | " |
| 307 | " | 12.1 | 345.7 | " |
| 310 | " | 10.7 | 305.7 | " |
| 317 | " | 9.5 | 271.4 | " |
| (309) | | (10.9) | (311.4) | |
| 266 | 550° 10 coats | 10.2 | 291.4 | 260.33 |
| 267 | " | 8.9 | 254.3 | " |
| 268 | " | 8.9 | 254.3 | " |
| 269 | " | 13.7 | 391.4 | " |
| 270 | " | 7.7 | 220.0 | " |
| 273 | " | 7.1(38 cycles) | 186.8 | " |
| 274 | " | 10.7 | 305.7 | " |
| 277 | " | 8.2 | 234.3 | " |
| 278 | " | 7.7 | 220.0 | " |
| 280 | " | 7.0 | 200.0 | " |
| 296 | " | 9.3 | 265.7 | " |
| 297 | " | 10.5 | 300.0 | " |
| 272 | 550° 20 coats | 8.1 | 231.4 | 275.72 |
| 276 | " | 8.9 | 254.3 | " |
| 279 | " | 6.6 | 188.6 | " |
| 283 | " | 8.5 | 242.9 | " |
| 286 | " | 7.3 | 208.6 | " |



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Table F1 (continued)

| Sample # | Spray Conditions | Wt. Loss (mg) | Wear Index | Avg.Wear Index |
|---|---|---|---|---|
| 287 | 550° 20 coats | 10.9 | 311.4 | 275.72 |
| 289 | " | 11.0 | 314.3 | " |
| 290 | " | 9.0 | 257.1 | " |
| 292 | " | 10.9 | 311.4 | " |
| 293 | " | 12.7 | 362.9 | " |
| 294 | " | 11.6 | 331.4 | " |
| 295 | " | 10.3 | 294.3 | " |
| 284 | 550° 40 coats | 23.9 | 682.9 | 629.02 |
| 285 | " | 23.2 | 662.9 | " |
| 327 | " | 21.5 | 614.3 | " |
| 330 | " | 22.8(37 cycles) | 616.2 | " |
| 331 | " | 19.5 | 557.1 | " |
| 332 | " | 21.5 | 614.3 | " |
| 334 | " | 23.9 | 682.9 | " |
| 335 | " | 21.7 | 620.0 | " |
| 336 | " | 21.3 | 608.6 | " |
| 338 | " | 24.1 | 688.6 | " |
| 339 | " | 20.0 | 571.4 | " |
| 355 | Uncoated, heat | 13.2 | 377.1 | 371.70 |
| 356 | treated 550° | 15.0 | 428.6 | " |
| 357 | 1 cycle (2 min) | 13.0 | 371.4 | " |
| 358 | " | 12.9 | 368.6 | " |
| 359 | Uncoated, heat | 13.3 | 380.0 | " |
| 360 | treated 550° | 12.8 | 365.7 | " |
| 361 | 5 cycles (2 min) | 15.9(40 cycles) | 397.5 | " |
| 362 | " | 11.4 | 325.7 | " |
| 365 | Uncoated, heat | 12.6 | 360.0 | " |
| 366 | treated 550° | 12.7 | 362.9 | " |
| 367 | 10 cycles (2 min) | 12.4 | 354.3 | " |
| 368 | " | 12.9 | 368.6 | " |



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TABLE F2

Statistical Analysis of the Abrasion Results t-Test

| Sample | $\bar{X}$ | $\bar{X}_u - X_c$ | df (degree of freedom) | S Variance | t | % of Confidence $\bar{X}$ uncoated > $\bar{X}$ coated |
|---|---|---|---|---|---|---|
| Virgin Uncoated Aluminum | 323.82 | - | - | 35.75 | - | - |
| 1 Coat | 254.51 | 69.31 | 22 | 20.90 | 5.8 | 99.9 |
| 5 Coats | 272.33 | 51.49 | 23 | 58.11 | 2.68 | 99.0 |
| 10 Coats | 260.33 | 63.49 | 22 | 53.89 | 3.42 | 99.9 |
| 20 Coats | 275.72 | 48.1 | 22 | 53.10 | 2.6 | 99.0 |
| 40 Coats | 629.02 | -305.2 | 21 | 44.82 | 18.3 | 99.9 |



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## APPENDIX G

High Temperature Oxidation Resistance
of $ZrO_2$ Films



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TABLE G1 - Heat Treatment Experiment

| Sample | Mat. Type | Furnace Temp ( C) | No. of Coating | Heat Treatment ( C) | Soaked Time at Temp(hrs) | Comments |
|---|---|---|---|---|---|---|
| 1-1 | 304ss | 650 | 1 | 1000 | 24 | Steel layer chipped off. |
| 1-2 | 304 | 650 | 1 | 1000 | 24 | Same as above. |
| 1-3 | 304 | 650 | 1 | 800 | 5 | Dark green |
| 1-4 | 304 | 650 | 1 | 800 | 5 | Brown |
| 2-1 | 304ss | 500 | 1 | 1000 | 24 | Steel layer chipped off. |
| 2-2 | 304 | 500 | 1 | 1000 | 24 | Same as above. |
| 2-3 | 304 | 500 | 1 | 800 | 5 | Dark green. |
| 2-4 | 304 | 500 | 1 | 800 | 5 | Brown and blue. |
| 4-1 | 310 | 600 | 5 | 1000 | 24 | Grey, no difference |
| 4-2 | 310 | 600 | 5 | 1000 | 24 | between coated and |
| 4-3 | 310 | 600 | 5 | 800 | 5 | uncoated samples. |
| 4-4 | 310 | 600 | 5 | 800 | 5 | Same as above. |
| 6-1 | 310 | 500 | 5 | 1000 | 24 | Same as above. |
| 6-2 | 310 | 500 | 5 | 1000 | 24 | Same as above. |
| 6-3 | 310 | 500 | 5 | 800 | 5 | Same as above. |
| 6-4 | 310 | 500 | 5 | 800 | 5 | Same as above. |
| 7-1 | 310 | 500 | 1 | 1000 | 24 | Brown. |
| 7-2 | 310 | 500 | 1 | 1000 | 24 | Dark blue-black |
| 7-3 | 310 | 500 | 1 | 800 | 5 | White coating remains |
| 7-4 | 310 | 500 | 1 | 800 | 5 | Blue |
| 8-1 | 310 | 500 | 1 | 1000 | 24 | No significant |
| 8-2 | 310 | 500 | 1 | 1000 | 24 | difference. |
| 8-3 | 310 | 500 | 1 | 800 | 5 | Same as above. |
| 8-4 | 310 | 500 | 1 | 800 | 5 | Same as above. |



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Table G1 (contd)

| Sample | Mat. Type | Furnace Temp (°C) | No. of Coating | Heat Treatment (°C) | Soaked Time at Temp(hrs) | Comments |
|---|---|---|---|---|---|---|
| 9-1 | 310 | 500 | 5 | 1000 | 24 | No significant |
| 9-2 | 310 | 500 | 5 | 1000 | 24 | difference. |
| 9-3 | 310 | 500 | 5 | 800 | 5 | Same as above. |
| 9-4 | 310 | 500 | 5 | 800 | 5 | Same as above. |
| 11-1 | 310 | 550 | 5 | 1000 | 24 | No difference between |
| 11-2 | 310 | 550 | 5 | 1000 | 24 | coated and uncoated |
| 11-3 | 310 | 550 | 5 | 800 | 5 | Same as above. |
| 11-4 | 310 | 550 | 5 | 800 | 5 | Same as above. |
| 14-1 | 310 | 600 | 5 | 1000 | 24 | Same as above. |
| 14-2 | 310 | 600 | 5 | 1000 | 24 | Same as above. |
| 14-3 | 310 | 600 | 5 | 800 | 5 | Same as above |
| 14-4 | 310 | 600 | 5 | 800 | 5 | Same as above. |
| 15-1 | 310 | 600 | 5 | 1000 | 24 | Same as above |
| 15-2 | 310 | 600 | 5 | 1000 | 24 | Same as above |
| 15-3 | 310 | 600 | 5 | 800 | 5 | Same as above |
| 15-4 | 310 | 600 | 5 | 800 | 5 | Same as above. |
| 16-1 | 310 | 600 | 1 | 1000 | 24 | Same as above |
| 16-2 | 310 | 600 | 1 | 1000 | 24 | Same as above |
| 16-3 | 310 | 600 | 1 | 800 | 5 | Same as above |
| 16-4 | 310 | 600 | 1 | 800 | 5 | Same as above |
| 18-1 | 310 | 700 | 1 | 1000 | 24 | Same as above |
| 18-2 | 310 | 700 | 1 | 1000 | 24 | Same as above |
| 18-3 | 310 | 700 | 1 | 800 | 5 | Same as above |
| 18-4 | 310 | 700 | 1 | 800 | 5 | Same as above |

Table G1 (contd)

| Sample | Mat. Type | Furnace Temp (°C) | No. of Coating | Heat Treatment (°C) | Soaked Time at Temp(hrs) | Comments |
|---|---|---|---|---|---|---|
| 19-1 | 310 | 700 | 5 | 1000 | 24 | No difference between |
| 19-2 | 310 | 700 | 5 | 1000 | 24 | coated and uncoated |
| 19-3 | 310 | 700 | 5 | 800 | 5 | samples. |
| 19-4 | 310 | 700 | 5 | 800 | 5 | Same as above |
| 20-1 | 310 | 700 | 5 | 1000 | 24 | Same as above |
| 20-2 | 310 | 700 | 5 | 1000 | 24 | Same as above |
| 20-3 | 310 | 700 | 5 | 800 | 5 | Same as above |
| 20-4 | 310 | 700 | 5 | 800 | 5 | Same as above |
| 25-1 | 310 | 550 | 5 | 1000 | 24 | No difference. |
| 25-2 | 310 | 550 | 5 | 1000 | 24 | Same as above. |
| 25-3 | 310 | 550 | 5 | 800 | 5 | Same as above |
| 25-4 | 310 | 550 | 5 | 800 | 5 | Same as above. |
| 26-1 | 310 | 550 | 3 | 1000 | 24 | Same as above |
| 26-2 | 310 | 550 | 3 | 1000 | 24 | Same as above |
| 26-3 | 310 | 550 | 3 | 800 | 5 | Same as above |
| 26-4 | 310 | 550 | 3 | 800 | 5 | Same as above |
| 29-1 | 310 | 550 | 3 | 1000 | 24 | No difference |
| 29-2 | 310 | 550 | 3 | 1000 | 24 | Same as above |
| 29-3 | 310 | 550 | 3 | 800 | 5 | Same as above |
| 29-4 | 310 | 550 | 3 | 800 | 5 | Same as above |



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TABLE G2

Heat Treatment Experiment of $ZrO_2$ Coated Samples

Temperature: 800°C, Soaked time: 1 hour, Sample Size: 1" x 1"

| Sample ID | $ZrO_2$ Coated | No. of Coats | Results |
|---|---|---|---|
| Nickel 16 | Coated | 3 | Samples remained the same. Heat treatment |
| " 16 | Uncoated | 0 | schedule was not sufficient to show the |
| " 17 | Coated | 3 | difference between coated and uncoated |
| " 17 | Uncoated | 0 | samples. Longer time and higher temper- |
| " 18 | Coated | 6 | ature are required. |
| " 18 | Uncoated | 0 | " |
| Carbon Steel 1 | Coated | 3 | All samples were destroyed. Steel pieces |
| " 1 | Uncoated | 0 | flaked off. The test schedule was too |
| " 10 | Coated | 3 | severe for carbon steel. No difference |
| " 10 | Uncoated | 0 | between coated and uncoated samples. |
| " 17 | Coated | 6 | " |
| " 17 | Uncoated | 0 | " |
| TiC Coated 4 | Coated | 3 | Significant improvement was observed in |
| Carbon Steel 4 | Uncoated | 0 | the $ZrO_2$ coated sample. For the uncoat- |
| " 5 | Coated | 6 | ed TiC steel, the TiC and steel layers |
| " 5 | Uncoated | 0 | flaked off while the $ZrO_2$ coated samples |
| | | | were not affected. |
| SS 304 15 | Coated | 10 | Samples started to show colour difference |
| " 15 | Uncoated | 0 | between coated and uncoated samples. |
| " 16 | Coated | 20 | Longer soak time is required. |
| " 16 | Uncoated | 0 | " |
| " 18 | Coated | 20 | " |
| " 18 | Uncoated | 0 | " |



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Fig. G1 Coated 310ss 1000$^{o}$ 24 hrs - 370x

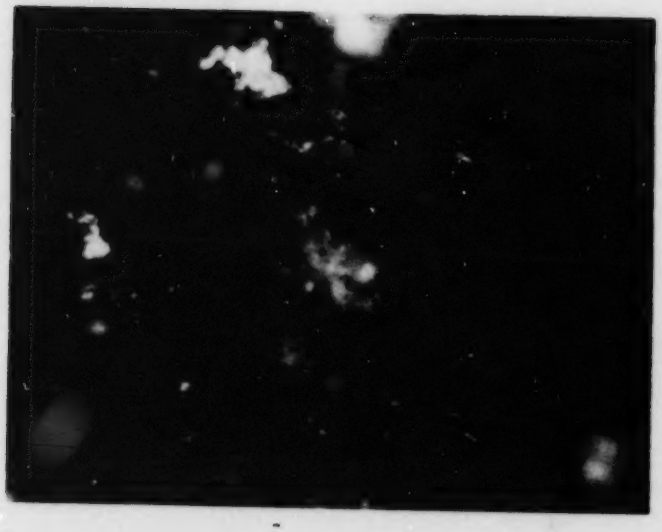

Fig. G2 Uncoated 310ss 1000$^{o}$C 24 hrs - 370x

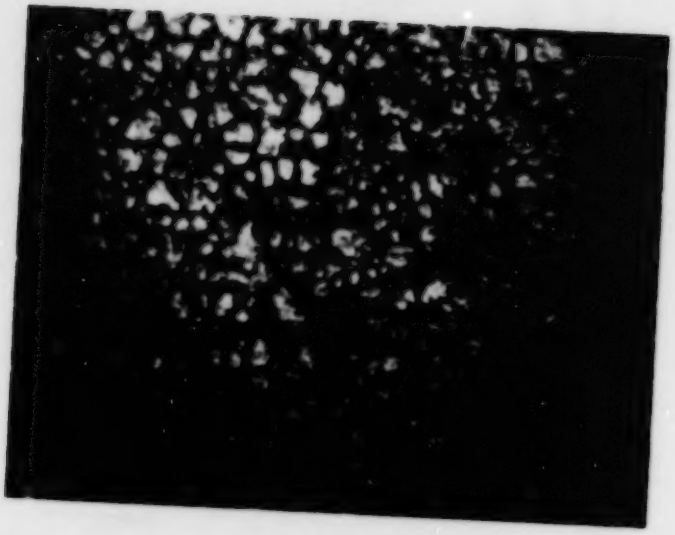

Fig. G3 Coated 304ss 800$^{o}$C 5 hrs - 370x

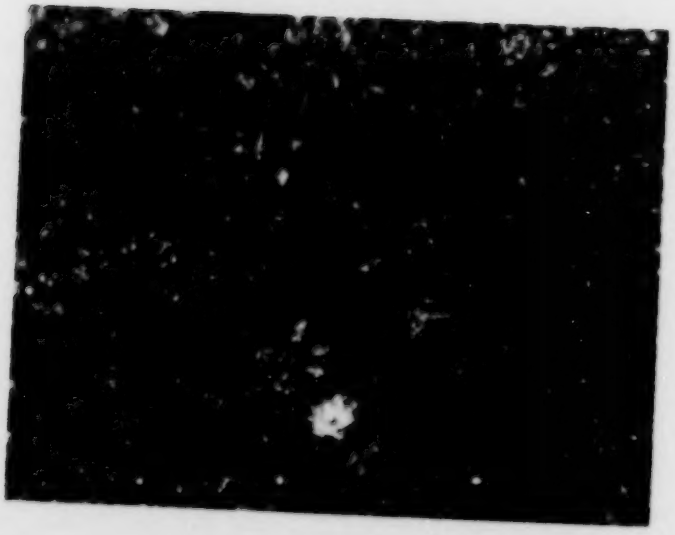

Fig. G4 Uncoated 304ss 800$^{o}$C 5 hrs - 370x

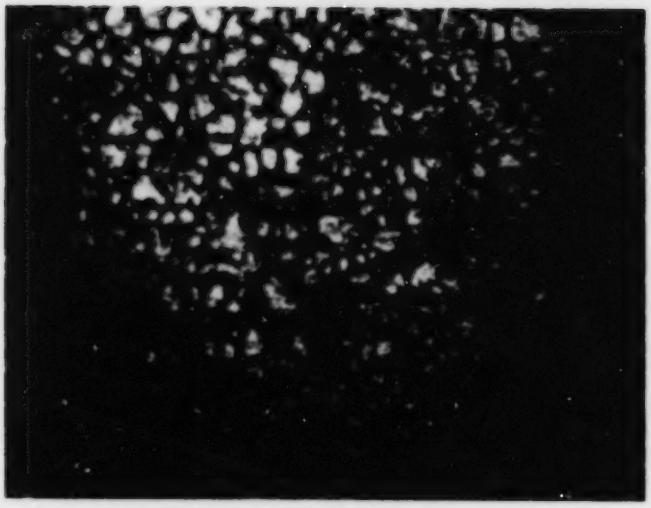

Fig. G3 Coated 304ss 800°C 5 hrs - 370x

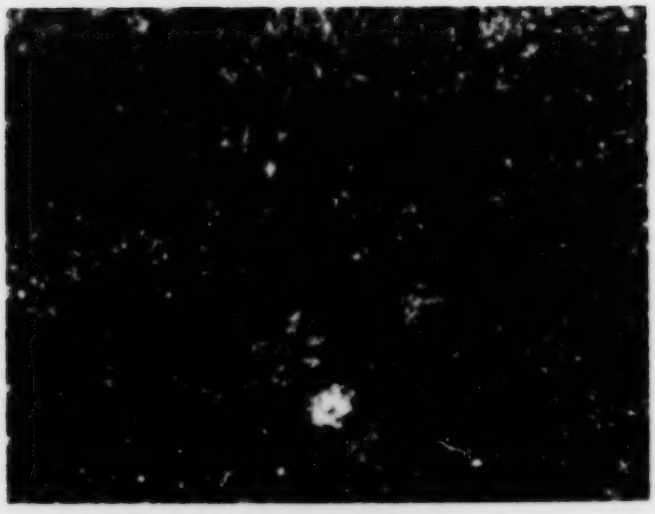

Fig. G4 Uncoated 304ss 800°C 5 hrs - 370x

## APPENDIX H

Alumina/Zirconia Mixed Films and Alumina Films



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## TABLE H1

### Zirconia/Alumina Coatings

| Sample # | Date | # Coats | Heat Treatment | Spray Time | Furnace Temp. | Results |
|---|---|---|---|---|---|---|
| Solution: 80% Butyl Zirconate 20% Al sec Butoxide | | | | | | |
| 651 | Jan.19/84 | 3 | 5 | 5 | 550 | Looks similar to $ZrO_2$ coating, but larger area. |
| 662 | " | 5 | 5 | 5 | 550 | Good coating, covers whole sample. |
| Solution 50% Butyl Zirconate 50% Al sec Butoxide | | | | | | |
| 663 | Jan.20/84 | 3 | 5 | 5 | 550 | Slightly cloudy, coloured rings faintly visible. |
| 664 | " | 6 | 5 | 5 | 550 | White coating, Newtons rings visible. |



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TABLE H2

Alumina Coatings (Al sec-Butoxide)

Solution: 70% Al sec Butoxide

30% Toluene

| Sample # | Date | # Coats | Heat Treatment (m) | Spray Time (s) | Furnace Temp. (°C) | Results |
|---|---|---|---|---|---|---|
| Substrate: Window Glass | | | | | | |
| 666 | Jan.20/84 | 3 | 5 | 5 | 650 | Transparent coating Newtons rings, glass broke. |
| 667 | " | 3 | 5 | 5 | 650 | Good coating, rings. |
| 668 | " | 3 | 2 | 2 | 550 | No visible coat. |
| 669 | " | 3 | 2 | 2 | 550 | " |
| 670 | " | 3 | 5 | 5 | 550 | Glass broke. |
| 671 | " | 3 | 5 | 5 | 550 | Very thin,Newton's rings |
| 672 | " | 10 | 5 | 5 | 550 | Slightly cloudy, rings visible. |
| 692 | Jan.27/84 | 6 | 3 | 5 | 550 | Thick, cloudy coating. |
| 693 | " | 6 | 3 | 2 | 550 | No visible coat. |
| 694 | " | 3 | 5 | 5 | 600 | Cloudy with rings around edges. |
| 695 | " | 6 | 5 | 5 | 600 | Cloudy coating, rings at edges. |
| Substrate: Stainless Steel 304 | | | | | | |
| 19 | Jan.27/84 | 3 | 3 | 5 | 700 | Light brown with rings. |
| 20 | Jan.30/84 | 3 | 3 | 5 | 700 | Yellow in middle, fine white powder. |
| 21 | " | 6 | 3 | 5 | 700 | Light brown, loose white powder on surface. |
| 22 | " | 3 | 3 | 5 | 600 | Dark coating, not transparent. |



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Table H2 (continued)

| Sample # | Date | # Coats | Heat Treatment (m) | Spray Time (s) | Furnace Temp. ($^{o}$C) | Results |
|---|---|---|---|---|---|---|
| 23 | Jan.30/84 | 6 | 3 | 5 | 600 | Problem with spray. |
| 24 | " | 3 | 3 | 5 | 500 | Dark brown coating. |
| 25 | " | 3 | 3 | 5 | 700 | Poor coating. |
| Substrate: TiC Coated Carbon Steel | | | | | | |
| TiC #11 | Jan.30/84 | 3 | 3 | 5 | 700 | Thin blue, white coating |
| Substrate: Nickel Plated Mild Steel | | | | | | |
| 37 | Jan.30/84 | 3 | 3 | 5 | 700 | Sample is green, coating white, barely visible. |
| 38 | " | 3 | 3 | 5 | 600 | Good coating, Newtons rings visible. |
| 39 | " | 6 | 3 | 5 | 600 | Similar to 38, white in centre. |
| Substrate: Aluminum | | | | | | |
| 370 | Jan.31/84 | 3 | 3 | 5 | 550 | Slightly cloudy, good coating, Newton's rings. |
| 373 | " | 6 | 3 | 5 | 550 | Thicker, powdery. |
| 376 | " | 3 | 3 | 5 | 600 | Good transparent coating |
| 377 | " | 6 | 3 | 5 | 600 | Cloudy, white powder formed on surface. |
| Substrate: Carbon Steel | | | | | | |
| 33 | Jan.31/84 | 6 | 3 | 5 | 600 | Brown, not transparent. |
| 34 | " | 3 | 3 | 5 | 600 | Black coating. |



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## APPENDIX I

## THE INDUSTRIAL POTENTIAL OF $ZrO_2$ COATINGS PRODUCED BY SPRAY PYROLYSIS



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## 1. Introduction

The use of surface coatings enhances the working life and performance capability of a component. The removal of as little as 0.1 - 0.2 mm from a machine part may reduce its operating efficiency. It has been estimated that about 30% of energy generated in all the industrial countries is consumed ultimately in friction/wear processes.

The application of a surface coating which protects the life span under rough, abrasive operation, may also reduce materials cost. The hard coating surface can be renewed easily when its service life is exhausted without the need for replacement of a whole component.

Ceramic coatings include those based on oxides, carbides, silicides, borides, nitrides, cermets and super porcelain. Ceramic coatings are also applied onto metals to protect them against oxidation and corrosion at room temperature and at elevated temperatures by one of two mechanisms. These coatings may protect metals at elevated temperatures. One type of coating is applied as a layer of stable oxide on the surface of the metal to prevent or delay contact between the metal and the atmosphere. The other type of ceramic coating is an intermetallic compound that forms a thin oxide film on its surface. The composition of the intermetallic is such that it provides the optimum combination of metallic elements for forming a stable and adherent protective oxide film on its surface.

Zirconia ($ZrO_2$) and alumina ($Al_2O_3$) are the oxides most commonly used as coating materials. Alumina coatings are hard and have excellent resistance to corrosion and abrasion. Zirconia has been widely used as a thermal barrier coating because of its low thermal conductivity.

## 2. The Application of $ZrO_2$ Films

$ZrO_2$ films may exist in three different crystal structures: cubic, tetragonal and monoclinic. According to El-Shashoury et al. [1], $ZrO_2$ films prepared by reactive evaporation exhibit the following transformations:



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$$ZrO_2 \text{ (quasiamorphous)} \xrightarrow{20\text{-}200^{\circ}C} ZrO_2 \text{(cubic)}$$

$$ZrO_2 \text{ (cubic)} \xrightarrow{500\text{-}600^{\circ}C} ZrO_2 \text{ (tetragonal)}$$

$$ZrO_2 \text{ (tetragonal)} \xrightarrow{900\text{-}1000 \text{ (vacuum)}} ZrO_2 \text{ (tetragonal + monoclinic)}$$

$$ZrO_2 \text{ (tetragonal + monoclinic)} \xrightarrow{1200\text{-}1300 \text{ (vacuum)}} ZrO_2 \text{ (monoclinic)}$$

$ZrO_2$ films can be prepared by many techniques such as plasma and flame spray, sputtering, chemical vapour deposition, evaporation, spray pyrolysis, anodization, hydrolysis, doctor blade and low temperature oxidation. All coating techniques were described in detail in the Phase I report (Appendix A Literature Review).

The potential applications of $ZrO_2$ films are mainly in two areas: thermal barrier coatings and in the electronic/optical fields. These different applications are dependent on the thickness and the structure of the deposited $ZrO_2$ films.

## 2.1 Thermal Barrier Coatings

Thermal barrier coatings are gaining importance in gas turbine engines as a means of increasing the system operating temperature. Yttrium-stabilized $ZrO_2$ applied by plasma spray is most commonly used. An increase in the service temperature of about 200°C has been demonstrated for this system. The initial development was restricted to stationary components but has now been extended to rotor blades.

Thermal barrier coatings applied to metals are effective, however, only in high heat flux situations, for example, when cooling is applied to the back surface or interior of a metallic component. If the heat generated is not absorbed, the temperature of the metal will approach that of the ceramic coating and no benefit will be gained.



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Zirconium coatings have also been applied to ceramic components to alter thermal response. For instance, zircon has been plasma sprayed on SiC in cases where low emissivity was required. The coating thickness by plasma spray for thermal barrier application is about 80-100 μ (0.08-0.1 mm)[3]. The structure of the plasma sprayed $ZrO_2$ film is usually monoclinic.

$ZrO_2$ coatings[4] have been applied to Inconel to promote a thermal insulating layer which slows down the rate of heat loss through the walls of a tube.

$ZrO_2$ films prepared by sol-gel technique have found application as beam-splitter anti-reflection coatings. These are particularly important for quartz and fluoride lamps [14]. Another application of $ZrO_2$ films is to provide coatings on a zirconia solid electrolyte for gas sensor control combustion engines or furnaces. After the addition of a Pt electrode, a second highly porous $ZrO_2$ coating is applied to prevent contamination by the environment. $ZrO_2$ films also increase the electrolyte surface area producing a structure which is highly responsive to changes in oxygen content in the gas stream being analyzed. The substrate can easily be recoated to increase the service life of the electrode.

Calcium-stabilized zirconia (CSZ) films have been noted for their application as anionic (oxygen) conductors at temperatures below 600°C. It was found that [5] thin CSZ films had solid electrolyte properties similar to those of the bulk electrolyte. This CSZ film could be used as oxygen anion conductor in the low temperature range from 200° to 600°C.

Thick zirconia films have been evaluated as the primary materials for high temperature seals [6]. Plasma sprayed $Y_2O_3$ stabilized $ZrO_2$ (YSZ) coatings have been deposited, 0.04 - 0.09 in. thick. The primer coat was a sputtered YSZ film for better adhesion. Buckley [7] found that the thermal properties of plasma-$ZrO_2$ coatings are linearly related to the coating thickness. Applications as heat barriers, and insulators in space vehicles and rockets are of special interest.

Thermal spray coatings of $Y_2O_3$-stabilized $ZrO_2$ for wear and corrosion resistance (detonation gun) have found application in Helium Cooled High Temperature Reactors (HTR). Plasma coatings of less than 25 $\mu$ [9] have been used in engines for thermal insulation and to improve corrosion resistance.

It has been noted by Bratton and Law [15] that zirconia thermal barrier coatings can increase the engine stability by reducing the operating temperature by 50°C to 200°C. The thickness of the $ZrO_2$ coating was about 600 $\mu$ and the primer coat of MCrAlY of about 100 $\mu$ thick. Applications of this type of coating are in aircraft engines, rocket and turbine engine components.

In summary, the thick zirconia coating ($\sim$100$\mu$) prepared by the flame and plasma spraying techniques is mainly used for thermal barrier and for corrosion portection. Wear resistance applications of thick $ZrO_2$ films although reported by several investigators are not common.

## 2.2 Electronic and Optical Applications

Ceramic coatings of $ZrO_2$ are needed in many applications requiring good thermal and/or electrical insulation. The coating techniques available for these applications are sputtering deposition, thermal spraying, CVD, anodization and pyrolytic deposition and hydrolysis.

Thin $ZrO_2$ was found to be corrosion resistant to many acids, e.g., phosphoric acid[10,11]. Thin $ZrO_2$ films are, therefore, potentially useful in corrosive environments. The properties of thin $ZrO_2$ films (0.05$\mu$ - 0.8$\mu$) such as a low dielectric constant and chemical inertness make them suitable for integrated circuit dielectric and insulation films.

$ZrO_2$ films prepared by CVD have been patented in 1973[12] for use as a passivation material with high electrical resistivity and very good impermeability to sodium. Sodium can be destructive to the circuit on a chip or wafer. $ZrO_2$ films are potential replacements for the commonly used $SiO_2$ films in electronic circuits due to their higher dielectric constant and greater impermeability to impurity diffusion.



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Other applications of thin $ZrO_2$ films are for thermal and electrical insulation, and for improved wear and erosion, corrosion, oxidation and sulfidation resistance of solar energy windows. The applications of $ZrO_2$ films have been summarized in Table 1.

3. The Properties of $ZrO_2$ Films Prepared by Spray Pyrolysis

Thin films of $ZrO_2$ prepared by the spray pyrolysis technique have several attractive properties. The film is transparent and can be deposited onto many clean and smooth substrates which can withstand the temperature range of about 500 to 600°C. The film is resistant to high temperature oxidation and is non-conductive. Other advantages of this deposition technique are its simple operation and low capital cost. Table 2 gives a summary of the properties of $ZrO_2$ films prepared by spray pyrolysis.

4. Industrial Potential of the Developed $ZrO_2$ Coatings

An attractive property of the thin $ZrO_2$ films deposited by spray pyrolysis is their potential applicability to a range of substrates which can withstand oxidation at temperatures between 500 and 600°C. These thin $ZrO_2$ films can, therefore, be used as the primer coat in applications where a strong and adherent undercoat is required.

The high temperature resistance of zirconia is also an advantage. Coating experiments with thin $ZrO_2$ films on TiC coated carbon steel (TiCS) indicated that the $ZrO_2$ film improved the heat resistance of the TiCS. This is an important property as the film can be applied as a secondary coat on TiC coatings to increase the working temperature of machine tools and bits.

The transparent nature of the thin $ZrO_2$ films enables the use of these films in many applications such as solar energy windows, electrical and thermal insulation films. Their non-conductivity is also an advantage. The $ZrO_2$ coating can be applied as a dielectric thin film in integrated circuits to replace silica film where sodium and impurity permeation

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appear to be a problem.

$ZrO_2$ films prepared by spray pyrolysis can be deposited onto solid $ZrO_2$ electrolytes which are being used as gas sensors in furnace combustion. Thin films of $ZrO_2$ can increase the surface area of the electrode for better sensitivity. In addition, this film can provide some protection for the expensive electrolyte in a severely contaminated environment and can be renewed easily when the coating layer is exhausted.

Moreover, the other advantages of the process are the low capital cost, ease of operation and low temperature required for the coating. The process can be carried out in the atmosphere.

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TABLE 1

Applications of $ZrO_2$ Coatings Prepared by Various Techniques.

| Technique | Coating | Application | Reference |
|---|---|---|---|
| Plasma-Arc Spraying | $ZrO_2$ | nuclear energy, jet engines MHD power generation. | 16 |
| " | Ni-Cr-Al-Y/ $ZrO_2$-$Y_2O_3$ | improve wear resistance in He-cooled high temperature reactors. | 8 |
| Flame Spraying | $ZrO_2$(CaO-Stab.) | thermal barrier coatings in aerospace vehicles. | 7 |
| " | $ZrO_2$ (Stab.) | to improve erosion resistance. | 17 |
| Sputtering | $ZrO_2$($Y_2O_3$-Stab.) | apply a primer between bondcoat and plasma sprayed YSZ to reduce laminar cracking. | 6 |
| " | $ZrO_2$(CaO-Stab.) | electronic insulators. | 5 |
| " | $ZrO_2$(pure, CaO-, $Y_2O_3$ -stab.) | thermal electrical insulation, reduced friction loss, increased wear or erosion resistance, protection from oxidation, sulfidation or corrosion. | 13 |
| CVD | $ZrO_2$ | insulating thin films. | 10 |
| " | $ZrO_2$ | MIS films. | 11 |
| Spray Pyrolysis | $ZrO_2$ | - | 2 |
| Hydrolysis | $ZrO_2$ | antireflection | 14 |
| Reactive Evaporation | $ZrO_2$ | thin films. | 1 |
| Doctor Blade Method | $ZrO_2$($Y_2O_3$-Stab.) | dense, translucent thin films. | 18 |

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